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Sol-Gel Preparation and Characterization of Non-Substituted and Sr-Substituted Lanthanum Cobaltates

Research Article

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Abstract: This paper reports on the results concerning the sol-gel preparation and characterization of Sr-substituted perovskite lanthanum cobaltates $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0.0, 0.25, 0.5 and 0.75). The metal ions, generated by dissolving starting materials in diluted acetic acid were complexed by 1,2-ethanediol to obtain the precursors for the non-substituted and Sr-substituted $LaCoO_3$. The influence of the synthesis temperature, heating time and the amount of substituent on the phase purity of $La_{1-x}Sr_xCoO_{3-\delta}$ were investigated. The phase transformations, composition and micro-structural features in the gels and polycrystalline samples were studied by thermal analysis (TG/DTA), infrared spectroscopy (IR), powder X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

Keywords: *Sol-gel synthesis • Perovskite cobaltates • $LaCoO_3$ • Strontium • Substitution effect*

1. Introduction

Perovskite ABO_3 and related materials are technologically important for many possible applications. This is a result of the variety of interesting properties of these compounds due to their compositional and structural diversity. Namely, these compounds exhibit ferroelectricity, pyroelectricity, ferromagnetism, superconductivity, colossal magnetoresistance, catalytic properties *etc.* [1-8], which render them as some of the most important technical materials. The perovskite $LaCoO_3$ system is a promising thermoelectric material due to its high Seebeck coefficient of 600 mV/K at room temperature. The thermopower of $LaCoO_3$ is positive due to the partial disproportionation $2Co^{3+} \leftrightarrow Co^{2+} + Co^{4+}$. Nevertheless the electrical resistivity is rather high which lowers the conversion efficiency. Lanthanum cobaltates are perovskites in which a proportion of A-site La cations may commonly be substituted by divalent atoms such as Ca or Sr [9-12]. They have high electron and ionic (O^{2-}) conductivities and are considered for use as cathode materials in solid oxide fuel cells, oxygen permeable membranes and are effective in catalytic oxidation of CO and hydrocarbons. The amount of charge carriers and thus the electrical conductivity and thermoelectric properties in this system can be tuned by suitable Co-site and La-site substitution [13-22]. There has been substantial recent interest in strontium-doped rare earth perovskites ($Ln_{1-x}Sr_xCoO_{3-\delta}$) as cathode materials for solid oxide fuels cells [19, 23-28], as an ideal substrate for the deposition of lead zirconium titanate (PZT) films [29], and as high temperature ceramic membranes [30-32]. These phases also display novel magnetic behaviour, including glassiness and room temperature ferromagnetism [33-42].

In the context of doped materials, the incorporation of homogeneously-distributed nanosized secondary phases in a host matrix, which can be realized by the molecular level fabrication of new materials, is of significant interest. In order to prepare these mixed oxides, the oxide-mixing method based on the solid state reaction between the component metal oxides is still utilized because of its lower manufacturing cost and simpler preparation process. This method, in general, however, requires the calcining temperature to be higher than 1000°C in order to eliminate the unreacted starting

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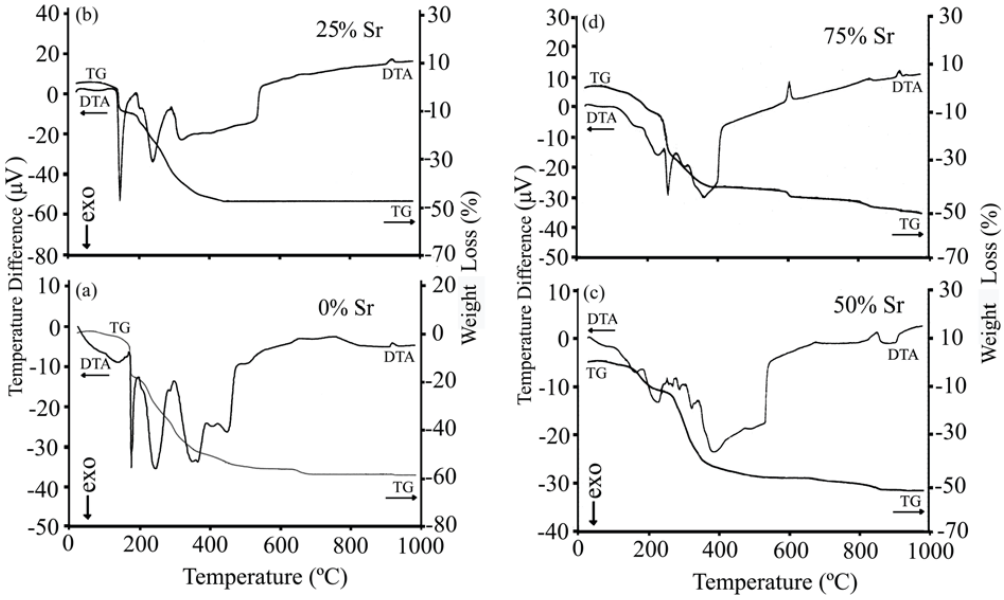

Figure 1. TG and DTA profiles of (a) La-Co-O, (b) La(0.75)-Sr(0.25)-Co-O, (c) La(0.5)-Sr(0.5)-Co-O, and (d) La(0.25)-Sr(0.75)-Co-O precursor gels. The heating rate was 10°C min^{-1}.

oxides and to obtain the final product as a single phase. In order to overcome these inevitable disadvantages arising from the solid state reaction, some methods including sol–gel, hydrothermal and coprecipitation techniques can be used.

Over the last few decades, the sol-gel techniques have been used to prepare a variety of mixed-metal oxides, nanomaterials and nanoscale architectures, nanoporous oxides, organic-inorganic hybrids [43-47]. Lanthanum cobaltate has been synthesized in the form of single crystals [48] and thin films by metal-organic chemical liquid [29] and chemical vapor deposition [49] techniques. For the preparation of bulk lanthanum cobaltate ceramics, different methods, such as solid state [50-52], co-precipitation [53,54], spray-pyrolysis [55], microemulsion [56], combustion [19,57,58] and reactive grinding [59] techniques could be used. Sol-gel chemistry routes using citric acid [18], EDTA [60] and glycine [61] as complexing agents were also suggested for the preparation of $LaCoO_3$-based ceramics. Recently for the preparation of different garnets, aluminates and superconductors, we elaborated an aqueous glycolate sol-gel processing route [62-67]. In this paper we present results of a systematic study of similar aqueous sol-gel synthetic approach to pure $LaCoO_3$ and Sr-substituted lanthanum cobaltates, $La_{1-x}Sr_xCoO_{3-\delta}$. The results illustrate the influence of annealing temperature, heating time and strontium concentration on the phase purity and crystallinity of the end products.

2. Experimental Procedures

2.1. Synthesis

Lanthanum cobaltate $LaCoO_3$ and lanthanum–strontium cobaltate $La_{1-x}Sr_xCoO_{3-\delta}$ (x = 0.0, 0.25, 0.5 and 0.75) ceramic samples were synthesized by an aqueous glycolate sol-gel method. The gels were prepared using stoichiometric amounts of analytical-grade lanthanum nitrate $La(NO_3)_3$, strontium nitrate $Sr(NO_3)_2$ and cobalt acetate tetrahydrate $Co(CH_3COO)_2{\cdot}4H_2O$ as La^{3+}, Sr^{2+} and Co^{3+} raw materials, respectively. For the preparation of unsubstituted samples by the sol-gel process, lanthanum nitrate was first dissolved in 50 mL of 0.2 mol L^{-1} CH_3COOH at 65°C. To this solution, cobalt acetate dissolved in 50 mL of distilled water was added and the resulting mixture was stirred for 1 h at the same temperature. For the preparation of Sr–substituted samples the appropriate amount of strontium nitrate dissolved in 50 mL of 0.2 mol L^{-1} CH_3COOH at 65°C was added and the resulting mixtures were stirred for 1 h at the same temperature. In a following step, 1,2-ethanediol (2 mL) as complexing agent was added to the reaction solution. After concentrating the solutions by a slow evaporation at 65°C under stirring, the La-Co-O or La(Sr)-Co-O nitrate-acetate-glycolate sols turned into mauve transparent gels. The oven dried (100°C) precursor gel powders were ground in an agate mortar and preheated for 5 h at 300°C and 3 h at 500°C in air. After grinding in an agate mortar, the powders were additionally sintered in air for 3 h and 10 h at 1000°C with an intermediate grinding.

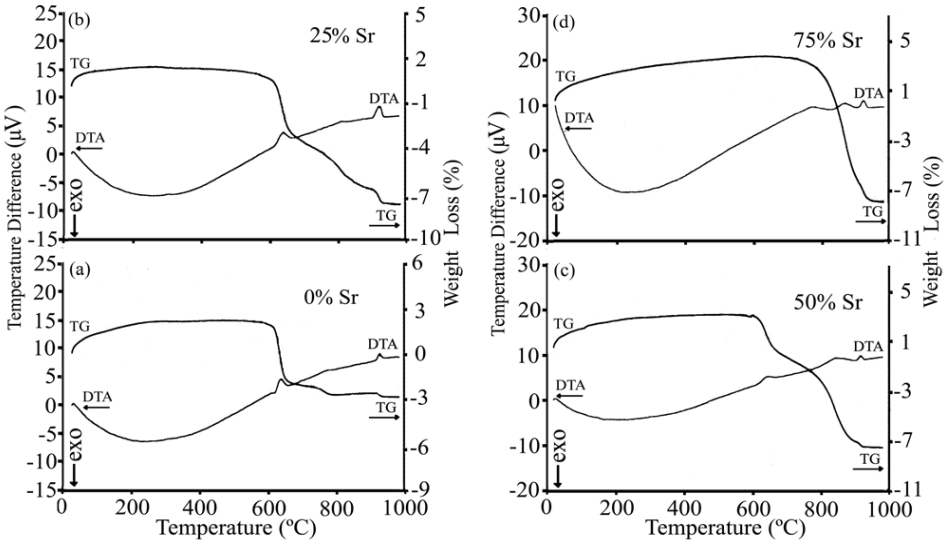

Figure 2. TG and DTA profiles of (a) $LaCoO_3$, (b) $La_{0.75}Sr_{0.25}CoO_{3-\delta}$, (c) $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (d) $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ materials obtained after heating the precursor gels for 5 h in 300°C and 3 h in 500°C. The heating rate was 5°C min^{-1}.

2.2. Measurements

The thermal decomposition processes of the precursor gels were studied in air atmosphere by thermogravimetric and differential thermal analyses (TG and DTA, respectively) using a Netzsch STA 409 thermal analyzer at a heating rate 5-10 °C min^{-1}. The infrared spectra in the range of 4000–400 cm^{-1} were recorded on an EQUINOX 55/S/NIR FTIR spectrometer. Samples were prepared as KBr pellets. Powder X-ray diffraction measurements were performed at room temperature on a Siemens D5000 diffractometer operating with CuK_α radiation. A scanning electron microscope (SEM) JEOL JSM 6400 was used to study the morphology and microstructure of the samples.

3. Results and Discussion

3.1. TG/DTA analysis

It is well known that thermal characterization of synthesized samples is important both for control of the reaction process and for the properties of the materials obtained. In this context, thermal analysis is a versatile aid to monitor preparative studies. The mechanism of the thermal decomposition of La-Co-O and La(Sr)-Co-O precursor gels in flowing air was studied by TG/DTA measurements. The TG/DTA profiles for the precursor gels are shown in Fig. 1. TG curves showed that in all cases the thermal decomposition proceeded in a similar way in that all the curves show two main weight losses in the temperature ranges ~20–200°C and ~200–500°C. Decomposition started below 200°C with a loss of crystallization water and/or water from the coordination sphere of the metal complexes. The observed weight loss between 200°C and 500°C is associated with thermal decomposition of nitrates, acetates and glycolates. The final weight loss on the TG curves of the gel samples was observed in the temperature range ~600-900°C, which indicates the formation of intermediate carbonates or oxycarbonates during pyrolysis of metal-organic components. The thermal decomposition behaviour is associated with endothermic and exothermic effects in the DTA curves.

The oven dried precursor gel powders were initially preheated for 5 h at 300°C and 3 h at 500°C in air. The TG/DTA curves for the intermediate products obtained at a heating rate of 5°C min^{-1} are shown in Fig. 2. The weight loss between 600–900°C is seen in all cases due to the decomposition of carbonate or oxycarbonate phases. Thus, it is obvious from the measurements that significant amounts of carbonate-containing phases (possibly $SrCO_3$, and $La_2O_2CO_3$) [6] have formed during the initial calcination of the La-Co-O and La(Sr)-Co-O precursor gel samples. This observation is corroborated by well-resolved endotherms in the DTA curves at approximately 600–650°C. Furthermore, well-resolved endotherms are also seen at around 900–920°C which must correspond to $LaCoO_3$ crystallization. Thus, according to the thermal analysis data, the crystallization of $LaCoO_3$ and $La_{1-x}Sr_xCoO_{3-\delta}$ ceramic oxides could vary from 900 to 1000°C. Therefore, the final annealing temperature of 1000°C for the sol-gel preparation of lanthanum cobaltate could be selected.

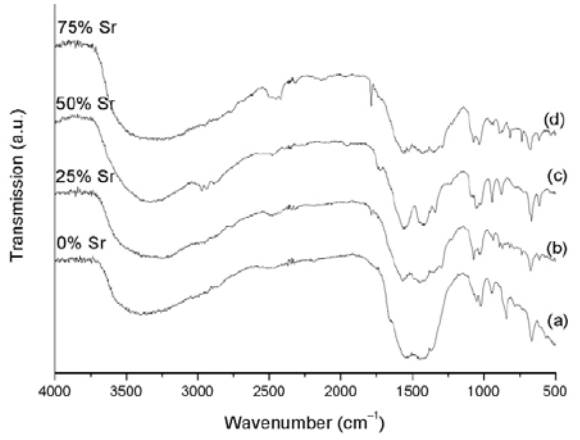

Figure 3. Infrared spectra of (a) La-Co-O, (b) La(0.75)-Sr(0.25)-Co-O, (c) La(0.5)-Sr(0.5)-Co-O, and (d) La(0.25)-Sr(0.75)-Co-O precursor gels.

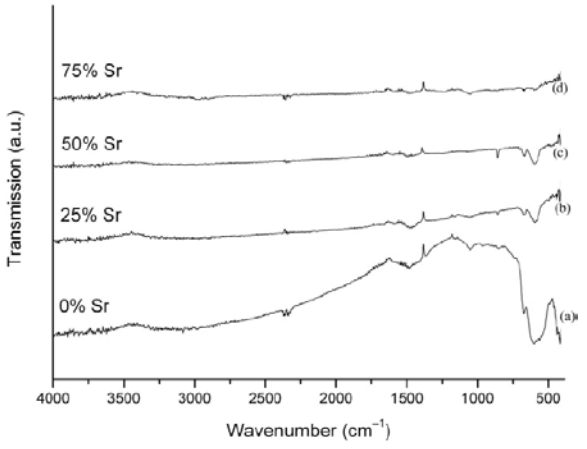

Figure 4. Infrared spectra of (a) $LaCoO_3$, (b) $La_{0.75}Sr_{0.25}CoO_{3-\delta}$, (c) $La_{0.5}Sr_{0.5}CoO_{3-\delta}$, and (d) $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ ceramics prepared at 1000°C.

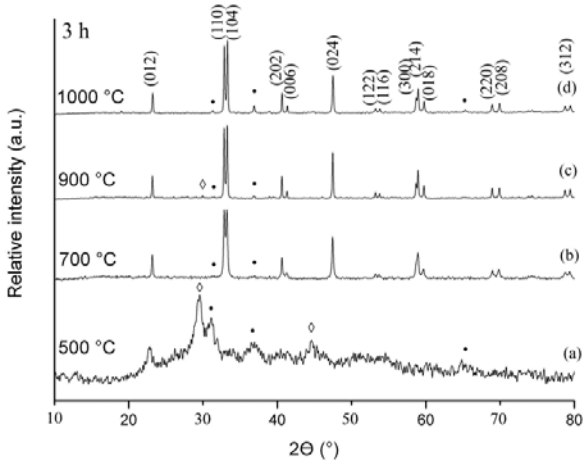

Figure 5. X-ray diffraction patterns of $LaCoO_3$ ceramics synthesized using the sol-gel method at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 3 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: • - Co_3O_4, ◊ - La_2O_3.

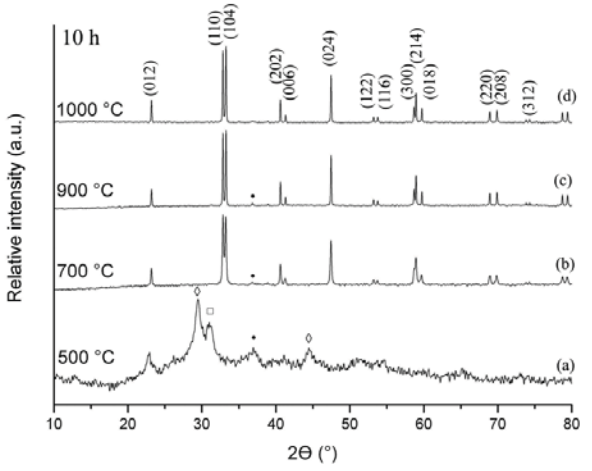

Figure 6. X-ray diffraction patterns of $LaCoO_3$ ceramics synthesized using the sol-gel method at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 10 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: □ - Co_2O_3, • - Co_3O_4, ◊ - La_2O_3.

3.2. IR spectroscopy

Fig. 3 shows the IR spectra of La(Sr)–Co–O precursor gels. As seen, all IR spectra are almost identical regardless of the strontium substitutional level. The bands observed in the IR spectra of the La(Sr)–Co–O gels schematically may be divided into four regions: 3700–2700, 1800–1300, 1200–900 and 800–500 cm^{-1}. Broad adsorption bands around 3400 cm^{-1} are the characteristic feature of absorbed water. The bands due to the CH_3 and CH_2 stretching can be observed at around 2900, 2800, and 1400 cm^{-1} whereas the strong bands at 3550-3200 (broad) and 1100–1050 cm^{-1} are due to CH_2-OH stretching [68]. The -CO-OH stretching frequencies can be identified at 1610–1600 and 1320–1290 cm^{-1}. A series of bands in the range 1700–1650, 1480–1450 and 950–910 cm^{-1} can be assigned to the nitrate groups [69,70]. Thus, it is not possible to state that only one precursor compound was formed; however, the IR and TG analyses of the gels show the 1,2-ethanediol, acetate and nitrate ligands to be present in the metal coordination spheres. Additionally, the IR bands at 800–550 cm^{-1} can be attributed to metal-oxygen M-O (possibly Co-O, Sr-O, La-O) vibrations [69,70]. Fig. 4 shows infrared spectra of the La(Sr)–Co–O gels heated at 1000°C. As seen, the IR spectra of samples calcined at 1000°C do not show any band attributable to carbonates, and only M–O stretching frequencies are observed. These results are consistent with the crystallization process observed by TG and X-ray diffraction measurements.

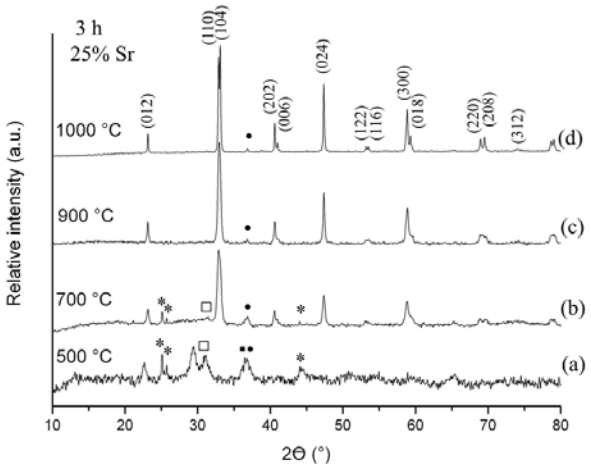

Figure 7. X-ray diffraction patterns of $La_{0.75}Sr_{0.25}CoO_{3-\delta}$ ceramics prepared at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 3 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: □ - Co2O3, • - Co3O4, ◊ - SrO, * - $SrCO_3$.

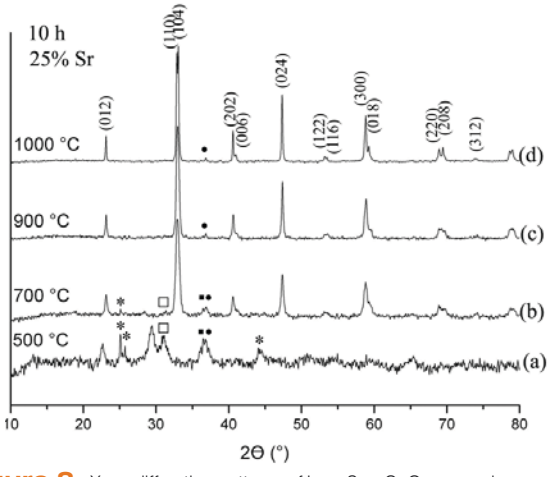

Figure 8. X-ray diffraction patterns of $La_{0.75}Sr_{0.25}CoO_{3-\delta}$ ceramics prepared at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 10 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: □ - Co_2O_3, • - Co_3O_4, ▪ - SrO, * - $SrCO_3$.

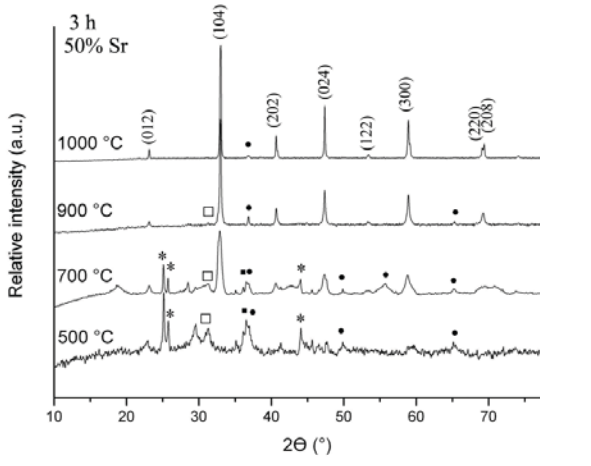

Figure 9. X-ray diffraction patterns of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ ceramics prepared at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 3 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: □ - Co_2O_3, • - Co_3O_4, ▪ - SrO, * - $SrCO_3$.

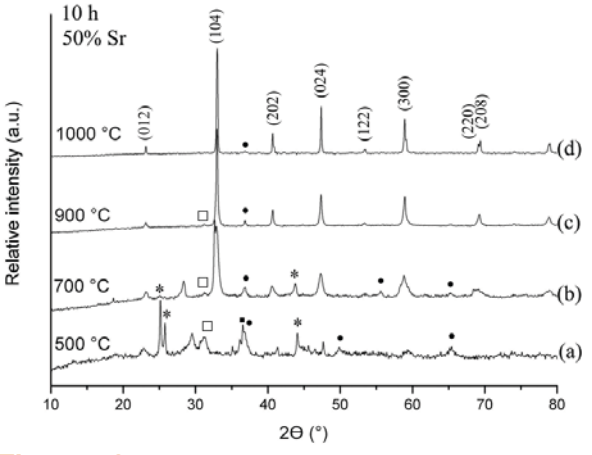

Figure 10. X-ray diffraction patterns of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ ceramics prepared at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 10 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: □ - Co_2O_3, • - Co_3O_4, ▪ - SrO, * - $SrCO_3$.

3.3. X-ray diffraction

The XRD patterns of $LaCoO_3$ ceramics heated at 500°C, 700°C, 900°C, 1000°C for 3 h and 10 h are shown in Figs. 5 and 6, respectively. According to the XRD analysis, a fully crystallized, almost single-phase oxide $LaCoO_3$ with the well pronounced perovskite crystal structure has formed already after annealing the precursor for 3 h at 700°C (see Fig. 5b) (JCPDS file 48–123). Impurity phases in the samples, attributable to Co_3O_4 (diffraction lines at $2\theta \approx 31.272, 36.853, 65.238$), and La_2O_3 ($2\theta \approx 29.961, 44.635$) however, also have been detected. With prolonged annealing time (10 h) the monophasic lanthanum cobaltate has formed at 1000°C (see Fig. 6).

The XRD patterns of the strontium-substituted $La_{0.75}Sr_{0.25}CoO_{3-\delta}$ sample heated at the same temperatures for 3 and 10 h are shown in Figs. 7 and 8, respectively. Evidently, the samples obtained at 700°C are multiphase materials despite the formation of perovskite phase already having started. The impurity phases in the samples can be attributed to Co_2O_3, Co_3O_4, and $SrCO_3$. The crystalline perovskite structure of strontium-substituted lanthanum cobaltate is obtained at higher temperature (900°C). The XRD data clearly confirm $La_{0.75}Sr_{0.25}CoO_{3-\delta}$ to be the main crystalline component, independent of the annealing time.

The XRD patterns of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ samples heated for 3 and 10 h are shown in Figs. 9-12. It may be seen that, with further increasing strontium substitutional level, the obtained

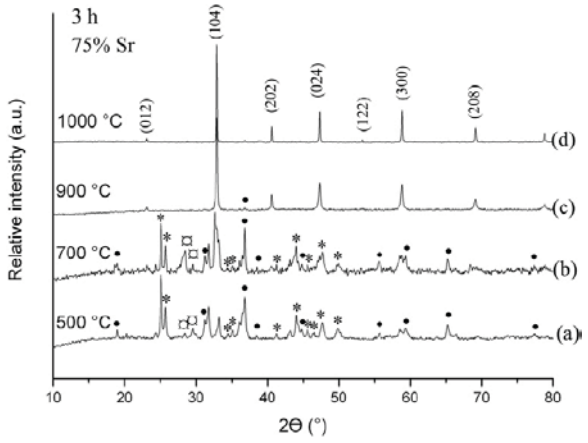

Figure 11. X-ray diffraction patterns of $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ ceramics prepared at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 3 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: • - Co_3O_4, * - $SrCO_3$, ¤ - unknown.

X-ray diffraction results are very similar. The formation of certain amounts of the impurity phases, such as SrO, $SrCO_3$, Co_2O_3, Co_3O_4, is evident at lower temperatures. Fully crystalline single-phase oxides $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ with the well pronounced perovskite crystal structure have formed at 900°C. This observation is opposite to the results obtained by investigating lanthanum [6] and gadolinium [71] substitution by strontium in perovskite aluminates. It was determined that when the Sr content is higher than 25%, the formation of perovskite lanthanum or gadolinium aluminates is problematic. It is interesting to note that the annealing time (3 and 10 h) has no influence on crystallinity and phase purity of $La_{1-x}Sr_xCoO_{3-\delta}$ oxides.

3.4. SEM analysis

Fig. 13 shows the SEM micrographs of oven dried La(Sr)–Co–O precursor gels. In all cases the scanning electron micrographs indicate the formation of monolithic gels. Fig. 14 shows the SEM micrographs of La(Sr)–Co–O gels heated at 1000°C. It is interesting to note that almost identical surface microstructure was observed for all ceramic samples. The particles of different shapes and sizes formed with very well pronounced agglomeration, indicating a good connectivity between the grains. The SEM micrograph suggests that the $La_{1-x}Sr_xCoO_{3-\delta}$ solids synthesized by the sol-gel route are composed of irregular submicron grains with an average grain size of less than 3 μm.

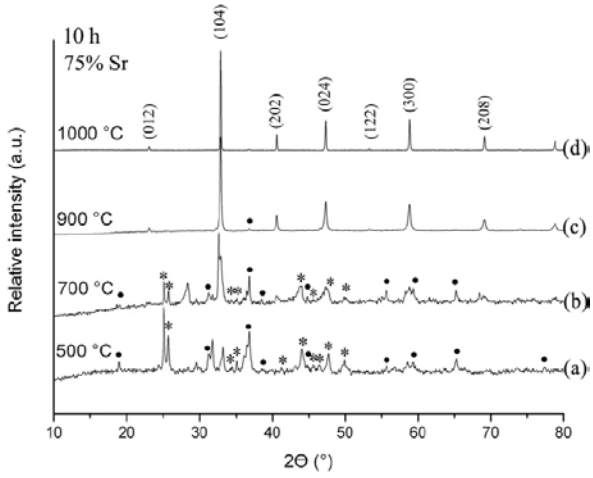

Figure 12. X-ray diffraction patterns of $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ ceramics prepared at different temperatures: (a) 500°C, (b) 700°C, (c) 900°C, (d) 1000°C. Annealing time was 10 h. The Miller indices of $LaCoO_3$ phase are marked. Impurity phases: • - Co_3O_4, * - $SrCO_3$.

4. Conclusions

From the present study it can be concluded that homogeneous gels in the La(Sr)-Co-O system were prepared by the complexation of metal ions with 1,2-ethanediol followed by a controlled hydrolysis and condensation in an aqueous media. The obtained gels have been used for the low-temperature synthesis of lanthanum cobaltate ($LaCoO_3$) and strontium-substituted lanthanum cobaltate ($La_{1-x}Sr_xCoO_{3-\delta}$) ceramics. The present study demonstrates the versatility of the solution method to yield a monophasic $LaCoO_3$ sample at low sintering temperature (up to 900-1000°C) when compared with the temperature required for the solid-state synthesis (>1400-1600°C). Furthermore, the Sr-substituted $La_{1-x}Sr_xCoO_{3-\delta}$ ceramics (up to 75% of Sr) also have been successfully obtained by this method. To our knowledge, $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ cobaltate with the perovskite structure has been prepared by a soft sol-gel chemistry approach for the first time. The annealing time was found to be an important parameter only for the nonsubstituted $LaCoO_3$ ceramics. Moreover, the proposed sol-gel method of preparation of lanthanum cobaltate in aqueous media is inexpensive and thus appropriate for the large scale production of ceramics of this type.

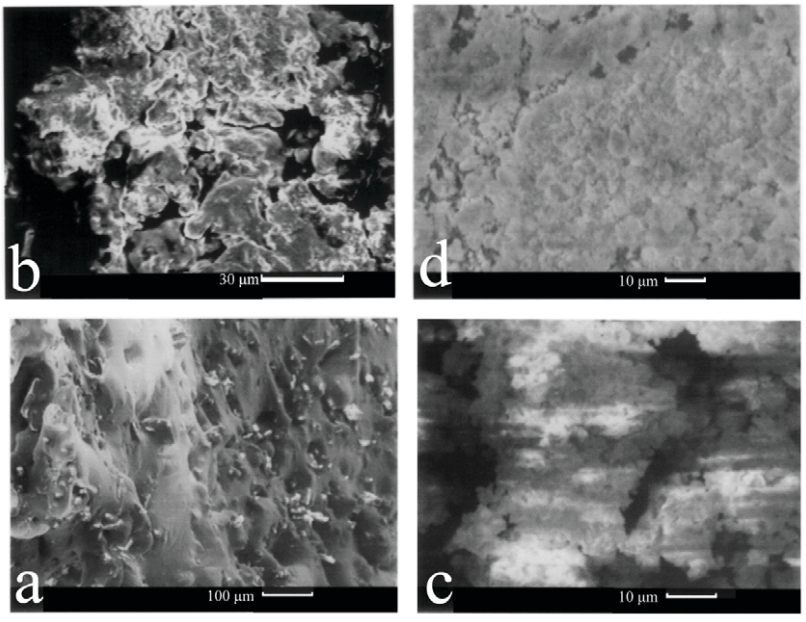

Figure 13. Scanning electron micrographs of (a) La-Co-O, (b) La(0.75)-Sr(0.25)-Co-O, (c) La(0.5)-Sr(0.5)-Co-O, and (d) La(0.25)-Sr(0.75)-Co-O precursor gels.

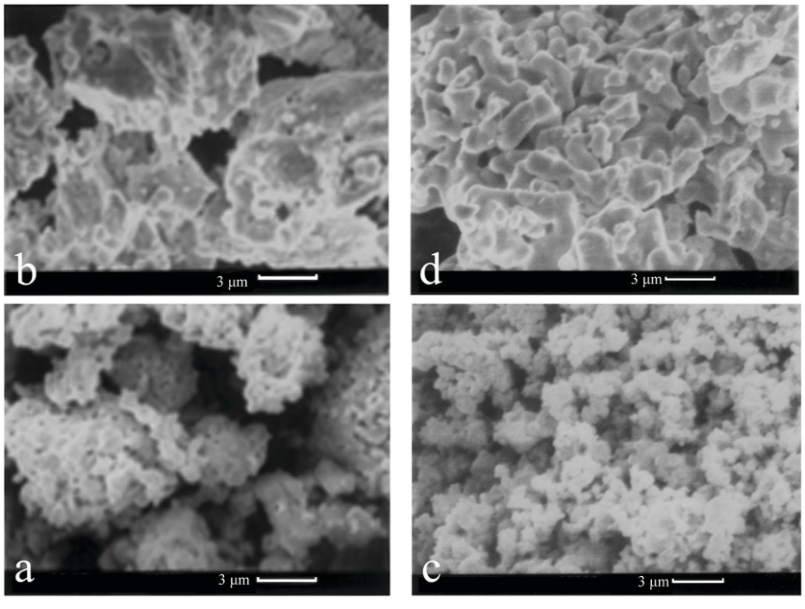

Figure 14. Scanning electron micrographs of sol-gel derived (a) $LaCoO_3$, (b) $La_{0.75}Sr_{0.25}CoO_{3-\delta}$, (c) $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (d) $La_{0.25}Sr_{0.75}CoO_{3-\delta}$ ceramics heated for 10 h at 1000°C.

Acknowledgements

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References

[1] F.S. Galasso, Perovskites and High Tc Superconductors, Gordon and Breach Science Publishers, New York, 1990
[2] E.J. Baran, Catal. Today 8, 133 (1990)
[3] L.B. Archer, C.D. Chandler, R. Kingsborough, M.J. Hampden-Smith, J. Mater. Chem. 5, 151 (1995)
[4] A.S. Bhalla, R. Guo, R. Roy, Mater. Res. Innov. 4, 3 (2000)
[5] J.P. Attfield, Int. J. Inorg. Mater. 3, 1147 (2001)
[6] M. Chroma, J. Pinkas, I. Pakutinskiene, A. Beganskiene, A. Kareiva, Ceram. Int. 31, 1123 (2005)
[7] M. Retuerto, J.A. Alonso, M.J. Martinez-Lope, N. Menedez, J. Tornero, M. Garcia-Hernandez, J. Mater. Chem. 16, 865 (2006)
[8] J. Zylberberg, Z.-G. Ye, J. Appl. Phys. 100, 086102 (2006)
[9] G. Thornton, B.C. Tofield, A.W. Hewat, J. Solid State Chem. 61, 301 (1986)
[10] J.C. Walmsley, A. Bardal, K. Kleveland, M.-A. Einarsrud, T. Grande, J. Mater. Sci. 35, 4251 (2000)
[11] J.A. Alonso, M.J. Martinez-Lope, C. de la Calle, V. Pomjakushin, J. Mater. Chem. 16, 1555 (2006)
[12] N.V. Minh, I.-S. Yang, Vibr. Spectrosc. 42, 353 (2006)
[13] M. Cherry, M.S. Islam, C.R.A. Catlow, J. Solid State Chem. 118, 125 (1995)
[14] C.H. Chen, H. Kruidhof, H.J.M. Bouwmeester, A.J. Burggraaf, J. Appl. Electrochem. 27, 71 (1997)
[15] A.A. Yaremchenko, V.V. Kharton, A.P. Viskup, E.N. Naumovich, V.N. Tikhonovich, N.M. Lapchuk, Solid State Ionics 120, 65 (1999)
[16] N. Orlovskaya, D. Ge, A. Nicholls, Key Eng. Mater. 206-213, 1321 (2002)
[17] B. Kucharczyk, W. Tylus, Catal. Today 90, 121 (2004)
[18] A. Kahoul, A. Hammouche, G. Poillerat, R.W. De Doncker, Catal. Today 89, 287 (2004)
[19] A. Patil, S. Dash, S.C. Parida, V. Venugopal, J. All. Comp. 384, 274 (2004)
[20] Z.Q. Deng, W. Liu, C.S. Chen, H. Lu, W.S. Yang, Solid State Ionics 170, 187 (2004)
[21] G,W. Chadzynski, D. Sternik, P. Staszczuk, B. Kucharczyk, J. Therm. Anal. Calorim. 78, 441 (2004)
[22] A. Weidenkaff, R. Robert, M. Aguirre, L. Bocher, T. Lippert, S. Canulescu, Renewable Energy 33, 342 (2008)
[23] J.L. Routbort, R. Doshi, M. Krumpelt, Solid State Ionics 90, 21 (1996)
[24] H.Y. Tu, Y. Takeda, N. Imanishi, O. Yamamoto, Solid State Ionics 100, 283 (1997)
[25] S.B. Adler, Solid State Ionics 111, 111 (1998)
[26] R.H.E. van Doorn, A.J. Burggraaf, Solid State Ionics 128, 65 (2000)
[27] S.J. Skinner, Int. J. Inorg. Mater. 3, 113 (2001)
[28] V.G. Prokhorov, Y.P. Lee, K.W. Kim, G.G. Kaminsky, V.M. Ishchuk, I.N. Chukanova, Mater. Sci. Forum 373-376, 605 (2001)
[29] G.S. Wang, X.J. Meng, Z.Q. Lai, J. Yu, J.L. Sun, J.G. Cheng, J. Tang, S.L. Guo, J.H. Chu, Appl. Phys. A 73, 1 (2001)
[30] A.V. Kovalevsky, V.V. Kharton, V.N. Tikhonovich, E.N. Naumovich, A.A. Tonoyan, O.P. Reut, L.S. Boginsky, Mater. Sci. Eng. B52, 105 (1998)
[31] V.V. Kharton, A.A. Yaremchenko, A.V. Kovalevsky, A.P. Viskup, E.N. Naumovich, P.F. Kerko, J. Membr. Sci. 163, 307 (1999)
[32] M. Sogaard, P.V. Hendriksen, M. Mogensen, F.W. Poulsen, E. Skou, Solid State Ionics 177, 3285 (2006)
[33] K. Asai, O. Yokokura, N. Nishimori, H. Chou, J.M. Tranquada, G. Shirane, S. Higuchi, Y. Okajima, K. Kohn, Phys. Rev. B 50, 3025 (1994)
[34] M.A. Senaris-Rodriguez, J.B. Goodenough, J. Solid State Chem. 118, 323 (1995)
[35] S. Mukherjee, R. Ranganathan, P.S. Anikumar, P.A. Joy, Phys. Rev. B 54, 9367 (1996)
[36] P.S. Anil Kumar, P.A. Joy, S.K. Date, J. Phys.: Condens. Matter 10, L487 (1998)
[37] D.N.H. Nam, K. Jonason, P. Nordblad, N.V. Khiem, N.X. Phuc, Phys. Rev. B 59, 4189 (1998)
[38] R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M.A. Senaris-Rodriguez, P.G. Radaelli, D. Fiorani, J.B. Goodenough, Phys. Rev. B 59, 1068 (1999)
[39] J. Mira, J. Rivas, M. Vazquez, J.M. Garcia-Beneytez, J. Arcas, R.D. Sanchez, M.A. Senaris-Rodriguez, Phys. Rev. B 59, 123 (1999)
[40] R. Ganguly, I.K. Gopalakrishnan, J.V. Yakhmi, Physica B 271, 116 (1999)
[41] S. Chaudhary, S.B. Roy, P. Chaddah, J. All. Comp. 326, 112 (2001)
[42] M. James, D. Cassidy, D.J. Goossens, R.L. Withers, J. Solid State Chem. 177, 1886 (2004)
[43] J. Livage, M. Henry, C. Sanchez, J. Solid State Chem. 18, 259 (1988)
[44] C.J. Brinker, G.W. Scherrer, Sol-gel science: the physics and chemistry of sol-gel processing, Academic Press, New York, 1990
[45] C. Sanchez, G.J.D.A.A. Soler-Illia, F. Ribot, D. Grosso, J. C. R. Chimie 6, 1131 (2003)
[46] B.L. Cushing, V.L. Kolesnichenko, C.J. O'Connor, Chem. Rev. 104, 3893 (2004)

[47] J.D Mackenzie, E.P. Bescher, Acc. Chem. Res. 40, 810 (2007)
[48] T. Ishigaki, S. Yamauchi, K. Kishio, J. Mizusaki, K. Fueki, J. Solid State Chem. 73, 179 (1988)
[49] Z.L. Wang, J. Zhang, Phil. Mag. A 72, 1513 (1995)
[50] A. Wold, R. Ward, Notes 30, 1029 (1954)
[51] M. Matsuda, K. Ihara, M. Miyake, Solid State Ionics 172, 57 (2004)
[52] F.J. Berry, J.R. Gancedo, J.F. Marco, X. Ren, J. Solid State Chem. 177, 2101 (2004)
[53] A.N. Jain, S.K. Tiwari, R.N. Singh, P. Chartier, J. Chem. Soc.-Faraday Transac. 91, 1871 (1995)
[54] T. Vaz, A.V. Salker, Mater. Sci. Eng. B 143, 81 (2007)
[55] S. Faaland, T. Grande, M.-A. Einarsrud, P.E. Vullum, R. Holmestad, J. Am. Ceram. Soc. 88, 726 (2005)
[56] M. Wallin, N. Cruise, U. Klement, A. Palmqvist, M. Skoglundh, Coll. Surf. A: Physicochem. Eng. Aspects 238, 27 (2004)
[57] W. Chen, F. Li, J. Yu, Mater. Lett. 61, 397 (2007)
[58] A. Baykal, N. Kasapoglu, Y. Koseoglu, A.C. Basarab, H. Kavas, M.S. Toprak, Cent. Eur. J. Chem. 6, 125 (2008)
[59] L. Huang, M. Bassir, S. Kaliaguine, Mater. Chem. Phys. 101, 259 (2007)
[60] N. Orlovskaya, K. Kleveland, T. Grande, M.-A. Einarsrud, J. Eur. Ceram. Soc. 20, 51 (2000)
[61] C.R. Dyck, Z.B. Yu, V.D. Krstic, Solid State Ionics 171, 17 (2004)
[62] E. Garskaite, K. Gibson, A. Leleckaite, J. Glaser, D. Niznansky, A. Kareiva, H.-J. Meyer, Chem. Phys. 323, 204 (2006)
[63] A. Zalga, A. Beganskiene, A. Kareiva, Polish J. Chem. 81, 1547 (2007)
[64] A. Katelnikovas, J. Barkauskas, F. Ivanauskas, A. Beganskiene, A. Kareiva, J. Sol-Gel Sci. Techn. 41, 193 (2007)
[65] S. Cizauskaite, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas, A. Kareiva. Mater. Chem. Phys. 102, 105 (2007)
[66] A. Katelnikovas, T. Justel, D. Uhlich, J.-E. Jorgensen, S. Sakirzanovas, A. Kareiva, Chem. Eng. Comm. 195, 758 (2008)
[67] A. Katelnikovas, A. Kareiva, Mater. Lett. 62, 1655 (2008)
[68] K. Nakanishi, Infrared Absorption Spectroscopy (Holden Day, San Francisco, 1977)
[69] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds (John Wiley and Sons, New York, 1986)
[70] B. Schrader, Infrared and Raman Spectroscopy. Methods and Applications (VCH, Weinheim, 1995)
[71] S. Cizauskaite, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas, A. Kareiva, Mater. Sci.-Poland 25, 755 (2007)