Sol-gel synthesis and structure of La$_2$O$_3$–CoO–SiO$_2$ powders

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Abstract

LaCoO$_3$ powders are studied because they exhibit interesting electrical, magnetic and catalytic properties. In this paper, new synthesized La$_2$O$_3$–CoO–SiO$_2$ powders with different quantity of silica were prepared via sol-gel method in aqua media, starting from metal nitrates with different chelating agents. The relation between the reaction in solution, crystallization pathway and morphology were discussed. In LaCoO$_3$–SiO$_2$ powders, depending on the content of SiO$_2$ and the treatment temperature (700–1100°C), different crystalline phases (LaCoO$_3$, Co$_2$SiO$_4$ and La$_{9.31}$(SiO$_4$)$_6$O$_2$) were observed with the crystallite sizes ranging from 50 to 100 nm. It was proved that chemical composition and nature of used additives has influence on the phase formation and structure of obtained nanomaterials.

Keywords: sol-gel synthesis, La$_2$O$_3$–CoO–SiO$_2$, powders

I. Introduction

Perovskite (LaMeO$_3$) type oxide comprising of rare earth ion and $d$-transition metal ions (Me), such as Fe, Mn, Co, Cr, Fe and Ni, has been increasingly applied to devices with improved electric and magnetic properties [1–4]. These compounds have also found application as catalysts for methane combustion reaction and CO oxidation [5]. LaCoO$_3$, as one very important member of this group, can be produced by using a lot of methods. Thus, „fused flux” route was used very frequently, but requires high temperatures and long calcination time [6–9]. To dissolve these hard limitations, other techniques were developed. Berger et al. [10] reported that pure and doped LaCoO$_3$ were obtained by solution combustion method with metal nitrates, and amino acid (alanine) or carbamide as fuel. Taguchi et al. [11,12] synthesized LaCoO$_3$ using poly(acrylic acid). They noticed that the amount of poly(acrylic acid) had strong influence on the morphology of obtained LaCoO$_3$ powder [14,15]. Citric acid and ethylene glycol have been used as chelating agents for preparing of LaCoO$_3$ structures, because they formed polymerizable complex, based on the processes of polyesterification [3,5,16,17]. A novel sol-gel method for preparations of LaCoO$_3$ powders with a Schiff base complex has also been developed by Worayyingong et. al. [18].

In addition to the pure LaCoO$_3$ very interesting system, from the application point of view, is La$_2$O$_3$–CoO–SiO$_2$. In the literature there is not enough information on the sol-gel synthesis, phase formation and structure evolution in this system. Thus, it would be interesting to obtain some new scientific data regarding the sol-gel processing of the La$_2$O$_3$–CoO–SiO$_2$, the formation of different crystalline phases and structure evolution depending on different silica content and calcination temperatures. We suppose that the presence of Si-O-Si network and different crystalline phases from La$_2$O$_3$–CoO system could provoke the synthesis of new nanocomposites with valuable catalytic, magnetic, electrical and optical properties.

In the present paper the recent results on the sol-gel synthesis and structure of perovskite-type LaCoO$_3$ and nanocomposites, obtained when different amount of SiO$_2$...
was added to La₂O₃·CoO, have been reviewed. The main goal is to establish the influence of chemical composition and used additives (chelating agents) on the phase formation and the structure evolution of synthesized materials. The crystallization processes in La₂O₃·CoO and La₂O₃·CoO with 10, 20 and 50 wt.% SiO₂ have been studied in order to obtain more information important for the synthesis of powders with desirable perovskite structure.

II. Experimental

Different LaCoO₃ powders were synthesized from La(NO₃)₆H₂O and Co(NO₃)₂·6H₂O in the presence of chelating agents: i) citric acid, ii) citric acid + polyethylene glycol (PEG), iii) carbamide and iv) glycine. The molar amount of chelating agent was equal to the total molar amount of metal nitrates in solution. The synthesis procedures were as follows: a weighed amount of La(NO₃)₆H₂O and chelating agent was dissolved in distilled water under magnetic stirring for 1h. It was necessary, because chelating agent may form ion associated “inner- and outer-sphere complex” with “clathrate coordination”. On one hand, this complex could prevent the aggregation of particles in the obtained mixed sol after adding cobalt salt. On the other hand, the presence of NO₃⁻, with its preference for bidentate coordination and its hard oxygen donors, has the greatest effect on the conformations of organic molecules used as chelating agent. A stoichiometric amount of Co(NO₃)₂·6H₂O was added into this inorganic-organic solution. After mixing for 2h, the reactants have formed a complete homogeneous transparent solution. Only the samples containing glycine were prepared with slowly addition of NH₄OH in order to adjust the pH value of the solution in the range of ~7–8 and to stabilize the nitrate-chelating agent solution. LaCoO₃ samples with different SiO₂ content were synthesized from La- and Co-nitrates (in the presence of carbamide) and tetraethoxysilane (TEOS). In the first step, using the sol-gel synthesis, TEOS was prehydrolysed in the presence of CH₃OH and H₂O using a volume ratio TEOS : CH₃OH : H₂O = 1 : 1 : 1. HCl was used as a catalyst. The hydrolysis reaction of TEOS was carried out under stirring to obtain a transparent silica containing solution. The prehydrolysed TEOS was added “drop to drop” to the La₂O₃-chelating agent-CoO solution. Three La₂O₃·CoO-SiO₂ sols with 10, 20 and 50 wt.% SiO₂ were prepared using the corresponding quantity of the prehydrolysed TEOS. Without any doubt, the polymerized silica network must rearrange the obtained mixed sol for obtaining good particle size distribution, which can lead to shorter periods of calcinations of the obtained dried gels.

The prepared sols (La₂O₃·CoO and La₂O₃·CoO with 10, 20 and 50 wt.% SiO₂) were gelled at 100°C/12h, and then heated at 150–250°C for another 12h. The obtained black amorphous powders were calcined in tubular furnace under an air flow in the temperature range from 700°C to 1100°C for 3h.

The phase formation and structure evolution of the obtained LaCoO₃ and LaCoO₃·SiO₂ powders have been studied by XRD (Bruker D8 Advance, in the 2θ range of 10–80°, CuKα radiation with energy dispersive Sol-X detector), FTIR (IR MATSON 7000-FTIR Spectrometer), TEM (EM-400, Philips) and SEM (JEOL JSM-550, JEOL JFC-1200 fine coater).

III. Results and Discussion

X-ray diffraction analysis – La₂O₃·CoO

The XRD patterns of the synthesized and thermal treated powders are given in Figs. 1–5. The XRD data interpretation was carried out by using JCPDF database.
From the obtained X-ray diffraction data, the crystallinity of samples was estimated by comparing the relative peak intensity of the corresponding crystalline phase. XRD patterns of the La$_2$O$_3$-CoO samples with different organic additives and thermal treated at 700°C/3h are given in Figs. 1 and 2. As can be seen in the presence of carbamide (Fig. 1a), glycine (Fig. 2a) and citric acid (Fig. 2b) the single-phase structure with perovskite LaCoO$_3$ phase (PDF 48-0123) was formed. XRD peaks of the samples prepared in presence of carbamide (Fig. 1a) and citric acid (Fig. 2a) have the highest intensity. The synthesized perovskite phase has the rhombohedral symmetry of LaCoO$_3$ crystal and nanoscaled size, which was calculated from Scherer’s formula and confirmed by TEM and SEM studies. The crystalline sizes obtained by X-ray line bordering were in the range of 50–100 nm depending on the chemical composition and treatment temperature.

Contrary to our results, Popa and Narihika [17] observed that when LaCoO$_3$ was synthesized via amorphous citrate method and thermal treatment at 650 and 700°C, XRD patterns of the obtained powder consist of some weak unidentified peaks other than LaCoO$_3$ phase. Our XRD data are in accordance with the results, presented by Predoana et al. [15], which synthesized LaCoO$_3$ powder, without the presence of other phases, using citric acid, metal acetates and nitrates, thermally treated at 600°C/6h. Worayingiong et al. [18], reported that the synthesized LaCoO$_3$ are characterized by high intensity peaks. The published results, from the same authors, showed no traces of La(OH)$_3$ and Co$_3$O$_4$ in the obtained LaCoO$_3$ powders. Bontempi et al. [19] also established, that the increasing in the annealing temperature at 700°C, resulted in the formation of crystalline pure LaCoO$_3$ without the presence of other phases, such as La$_2$O$_3$, La(OH)$_3$, CoO and Co$_3$O$_4$. From the published results it can be seen, that the La$_2$O$_3$ phase would have been observed after annealing the sample at 1000°C [19]. In the case of citric acid and ethylene glycol, Taguchi et al. [5] reported that the LaCoO$_3$ is a main crystalline phase in the synthesized samples.

On the other hand, in the La$_2$O$_3$-CoO powders, synthesized in the presence of citric acid + PEG and heat treated at 700°C/3h (Fig. 1b), CoO (PDF 48-1719) appears as a secondary phase. The dominant LaCoO$_3$ phase has low intensity peaks.

XRD patterns of the LaCoO$_3$, synthesized in the presence of carbamide, glycine and citric acid + PEG, thermally treated at 900°C/3h are presented in Fig. 3. The pure LaCoO$_3$ phase is observed for the samples prepared in the presence of carbamide (Fig 3a) and glycine (Fig. 3b). However, Co$_3$O$_4$ (PDF 42-1467), can be detected in the La$_2$O$_3$-CoO powder synthesized with citric acid + PEG (Fig. 3c). It can be also seen that the intensity of the LaCoO$_3$ peaks depends on the type of the used chelating agents, and decreases as follows: carb-
amide > citric acid + PEG > glycine. The obtained results are in a good agreement with those published by Matei et al. [20], in which LaCoO$_3$ was observed as a main phase in the presence of alkali metal chlorides as molten salts thermally treated at 950°C for 24 h.

**X-ray diffraction analysis – La$_2$O$_3$-CoO-SiO$_2$**

Very interesting new data could be recognised from XRD patterns of the synthesized LaCoO$_3$-SiO$_2$ powders (in the presence of carbamide) after thermal treatment at 900°C and 1100°C/3h (Figs. 4 and 5). The prepared LaCoO$_3$-SiO$_2$ powders, depending on the content of SiO$_2$ and the treatment temperature (700–1100°C), consist of different crystalline phases: LaCoO$_3$, Co$_3$SiO$_4$ (PDF 29-0508) and La$_{1.31}$Si$_2$O$_7$ (PDF 76-0340). Thus, in the LaCoO$_3$ with 10 wt.% SiO$_2$ the dominant perovskite LaCoO$_3$ is accompanied with two other phases - CoSiO$_4$ and La$_{9.31}$Si$_4$O$_2$. It can be also seen from Fig. 4 that the quantity of secondary silicate phases decreases with increasing temperature from 900°C to 1100°C.

In comparison to the LaCoO$_3$ + 10 wt.% SiO$_2$, X-ray diffraction patterns of the LaCoO$_3$ + 20 wt.% SiO$_2$ samples are quite different (Fig. 5). As can be seen, in the LaCoO$_3$ + 20 wt.% SiO$_2$ powder treated at 900°C for 3h, the perovskite LaCoO$_3$ is still the dominant phase (Fig. 5a) and a small portion of Co$_3$SiO$_4$ and La$_{9.31}$Si$_4$O$_2$ can be also observed. However, the LaCoO$_3$ +20 wt.% SiO$_2$ powder treated at 1100°C/3h, consists of orthorhombic Co$_3$SiO$_4$ as the major phase, with only a very small portion of other phases, such as: LaCoO$_3$ and Co$_3$O$_4$.

It is important to mark that the average crystalline size of the LaCoO$_3$ phase in the LaCoO$_3$ + 10 wt.% SiO$_2$ powder is calculated to be about 50 nm and 85 nm at 900°C and 1100°C, respectively. However, in the case of the LaCoO$_3$ + 20 wt.% SiO$_2$ powder, thermally treated at 900°C/3h, the size of LaCoO$_3$ crystallite increases to 100 nm.

The XRD patterns of the LaCoO$_3$ + 50 wt.% SiO$_2$ powder (the data are not shown here), thermally treated at 1100°C/3h, indicate a very complicated phase composition with the presence of different oxides and silicates of lanthanum and cobalt.

**Fourier transform infrared spectroscopy (FTIR)**

The structure of sol-gel synthesized LaCoO$_3$ and LaCoO$_3$ + 10, 20 and 50 wt.% SiO$_2$ was studied by FTIR (Fig. 6). The FTIR spectrum of the LaCoO$_3$ powder, heat treated at 900°C/3h, has three characteristic bands at 422, 597 and 678 cm$^{-1}$. The two strong absorption bands at about 590 and 678 cm$^{-1}$ are assigned to Co-O stretching vibration and O-Co-O deformation modes of LaCoO$_3$, respectively [18,21].

La-O bond was assigned to the presence of the absorption band at around 415–423 cm$^{-1}$ [22]. The FTIR spectra are changed considerably with addition of SiO$_2$ (Fig. 6). Thus, in the case of the nanocomposite containing 50 wt% SiO$_2$, the FTIR spectrum (Fig. 6d) shows the
bands at 950 cm\(^{-1}\), attributed to Si-OH groups and 1004 cm\(^{-1}\) assigned to \(v_{\text{as}}\) Si-O-Si stretching vibration. This bond shifts to lower wave number in the nanocomposite with 10 wt.% SiO\(_2\). The FTIR spectrum of the La\(_{2-x}\)-CoO powder with 10 wt.% SiO\(_2\), treated at 900°C and 1100°C for 3h (Fig. 6b,c) shows the strong chemical bond at 1484 cm\(^{-1}\) can also be observed. This bond could be assigned to Co-O stretching vibrations [23].

**Scanning Electron Microscopy (SEM)**

The morphology of the particles in the obtained La\(_{2-x}\)-CoO-SiO\(_2\) powders after calcination at different temperatures is determined by SEM (Fig. 7) and TEM (Fig. 8) observations. It is established that the particle size varies from 70–100 nm (for crystallites) to 1 μm (for aggregates) and their shape depends on the sample composition and heat treatment temperature. Only in the sample LaCoO\(_3\) + 20 wt.% SiO\(_2\) the particles are with nanoscale sizes, without aggregation trend and with a lower contrast image.

**IV. Conclusions**

Different LaCoO\(_3\) powders were prepared by the sol-gel technique from lanthanum and cobalt nitrates and in the presence of chelating agents: i) citric acid, ii) citric acid + polyethylene glycol (PEG), iii) carbamide and iv) glycine. LaCoO\(_3\), single phase composition with rhombohedral distorted perovskite structure is observed in the sol-gel samples prepared in the presence of carbamide, citric acid and glycine, and thermal treated at 700°C and 900°C. From the depicted XRD data the high intensity peaks of the obtained LaCoO\(_3\), after thermal treatment at 900°C, are decreased as follows: carbamide > citric acid + PEG > glycine.

New nanocomposites of the La\(_2\)-CoO-SiO\(_2\) system with 10, 20 and 50 wt.% SiO\(_2\) were synthesized via modified sol-gel method. The obtained powders were prepared from lanthanum and cobalt nitrates, carbamide, TEOS, CH\(_3\)OH, H\(_2\)O and HCl. In the synthesized LaCoO\(_3\)-SiO\(_2\) powders, depending on the content of SiO\(_2\) and treatment temperature (700–1100°C) different crystalline phases, such as LaCoO\(_3\), Co\(_3\)SiO\(_7\) and La\(_{2/3}\)(SiO\(_4\))\(_{2/3}\) are observed. LaCoO\(_3\) is indicated as a main crystalline phase, which is accompanied with two other phases - CoSiO\(_3\) and La\(_{2/3}\)(SiO\(_4\))\(_{2/3}\) for the samples: LaCoO\(_3\) + 10 wt.% SiO\(_2\) thermally treated at 900°C and 1100°C, and LaCoO\(_3\) + 20 wt.% SiO\(_2\) at 900°C. On the other side, the sample LaCoO\(_3\) + 20 wt.% SiO\(_2\) treated at 1100°C has the orthorhombic CoSiO\(_3\) as a dominant phase. The crystallite sizes of the obtained phases are from 50 to 100 nm. Taking into consideration the chemical and phase compositions, as well as their structure, it is supposed that new sol-gel nanocomposites possess valuable catalytic, magnetic, electrical and optical properties.

It has been proved the influence of chemical composition and nature of used additives on the phase formation and structure of obtained La\(_2\)-CoO and La\(_2\)-CoO-SiO\(_2\) nanomaterials.

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**References**


