

**VILNIUS UNIVERSITY**

Sigutė Čižauskaitė

**SOL-GEL SYNTHESIS OF PEROVSKITE STRUCTURE  
ALUMINATES AND COBALTATES**

**Summary of doctoral dissertation**

Physical sciences, Chemistry (03 P)

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**Scientific supervisors:**

Prof. dr. Aldona Beganskienė (Vilnius University, Physical Sciences, Chemistry, 03 P); (2005–2006 m.); Prof. habil. dr. Aivaras Kareiva (Vilnius University, Physical Sciences, Chemistry, 03 P); (2007–2009 m.).

**Scientific consultant:**

Prof. dr. Jiri Pinkas (Masaryk University Brno, Physical Sciences, Chemistry, 03 P).

**Evaluation board:**

**Chairman:**

Prof. habil. dr. Rimantas Ramanauskas (Institute of Chemistry, Physical Sciences, Chemistry, 03 P);

**Members:**

Prof. dr. Jurgis Barkauskas (Vilnius University, Physical Sciences, Chemistry, 03 P);

Prof. dr. Jadvyga Regina Kerienė (Vilnius Gediminas Technical University, Technological Sciences, Materials Engineering, 08 T);

Prof. habil. dr. Arūnas Ramanavičius (Vilnius University, Physical Sciences, Chemistry, 03 P);

Dr. Julija Razumienė (Institute of Biochemistry, Physical Sciences, Chemistry, 03 P).

**Official opponents:**

Prof. habil. dr. Vitalijus Janickis (Kaunas University of Technology, Physical Sciences, Chemistry, 03 P);

Dr. Artūras Žalga (Vilnius University, Physical Sciences, Chemistry, 03 P).

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Address: Naugarduko 24, LT-03225 Vilnius, Lithuania. Tel. 2193108. Fax: 2330987.

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**VILNIAUS UNIVERSITETAS**

Sigutė Čižauskaitė

**PEROVSKITO STRUKTŪROS ALIUMINATŲ IR  
KOBALTATŲ SINTEZĖ ZOLIŲ-GELIŲ METODU**

**Daktaro disertacijos santrauka**

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**Moksliniai vadovai:**

prof. dr. Aldona Beganskienė (Vilniaus universitetas, fiziniai mokslai, chemija, 03 P);  
(2005–2006 m.);

prof. habil. dr. Aivaras Kareiva (Vilniaus universitetas, fiziniai mokslai, chemija, 03 P);  
(2007–2009 m.).

**Mokslinis konsultantas:**

Prof. dr. Jiri Pinkas (Masaryk'o Brno universitetas, fiziniai mokslai, chemija, 03 P).

**Disertacija ginama Vilniaus universiteto Chemijos mokslo krypties taryboje:**

**Pirmininkas:**

Prof. habil. dr. Rimantas Ramanauskas (Chemijos institutas, fiziniai mokslai, chemija,  
03 P);

**Nariai:**

Prof. dr. Jurgis Barkauskas (Vilniaus universitetas, fiziniai mokslai, chemija, 03 P);

Prof. dr. Jadvyga Regina Kerienė (Vilniaus Gedimino technikos universitetas,  
technologijos mokslai, medžiagų inžinerija, 08 T);

Prof. habil. dr. Arūnas Ramanavičius (Vilnius universitetas, fiziniai mokslai, chemija, 03  
P);

Dr. Julija Razumienė (Biochemijos institutas, fiziniai mokslai, chemija, 03 P).

**Oponentai:**

Prof. habil. dr. Vitalijus Janickis (Kauno technologijos universitetas, fiziniai mokslai,  
chemija, 03 P);

Dr. Artūras Žalga (Vilniaus universitetas, fiziniai mokslai, chemija, 03 P).

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Adresas: Naugarduko 24, LT-03225 Vilnius, Lietuva. Tel.:2193108. Faksas: 2330987.

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## 1. INTRODUCTION

The development of innovative multi-functional advanced materials should have a major impact in future applications. Perovskite 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.*, which render them as some of the most important technical materials. These properties mainly depend on the crystal size, defects, surface and interface properties. That's why the preparation of pure, stoichiometric, homogeneous and crystalline perovskite materials is of high interest.

Perovskite-type complex oxides are well known as functional inorganic materials for application as electrode materials in solid oxide fuel cells (SOFCs), gas sensors, membranes for separation and catalysts *etc.* Ceramics based on  $Ln_2O_3-Al_2O_3$  ( $Ln$  – lanthanide element) combination are promising materials for optical, magnetic, electronic and structural applications. The perovskite aluminates doped with lanthanide element offers advantages of longer lifetimes and higher, polarized cross sections with respect to most of other oxide matrices, and are useful as host for solid-state lasers, luminescence systems and window materials for a variety of lamps. Related ceramic materials are currently being incorporated into automobile catalytic converters, also are promising substrates for the epitaxy of thin oxide films having potential use as buffer layers for the epitaxial growth of various perovskite-type films such as a high temperature superconductors, ferroelectrics and colossal magnetoresistance oxides.

There has been studied cobalt-containing perovskites  $LnCoO_3$  ( $Ln = La, Pr, Nd, Sm$  and  $Gd$ ) as catalyst precursors for the partial oxidation of methane to synthesis gas.

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, as an ideal substrate for the deposition of lead zirconium titanate (PZT) films, and as high temperature ceramic membranes. These phases also display novel magnetic behaviour, including glassiness and room temperature ferromagnetism.

Owing to such wide applications of perovskite ceramics, new environmentally friendly, economical simple routes for the synthesis of these materials are highly desirable. 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 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.

In this study we report results of a systematic study of similar aqueous sol-gel synthetic approach to pure gadolinium aluminate ( $\text{GdAlO}_3$ ) lanthanum and gadolinium cobaltates ( $\text{LaCoO}_3$ ,  $\text{GdCoO}_3$ ) and Sr-substituted gadolinium aluminates ( $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{AlO}_{3-\delta}$ ), lanthanum and gadolinium cobaltates ( $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ ). The results illustrate the influence of starting material, complexing agent, annealing temperature, heating time and strontium concentration on the phase purity and crystallinity of the end products.

**The main aim of this work was** to synthesize and investigate perovskite structure compounds. For this reason there were formulated tasks as follows:

1. Development of sol-gel technique for the preparation of monophasic perovskite structure gadolinium aluminate ( $\text{GdAlO}_3$ ), lanthanum and gadolinium cobaltate ( $\text{LaCoO}_3$ ,  $\text{GdCoO}_3$ ) ceramics.
2. Investigation of strontium substitution effect in perovskite structure gadolinium aluminates ( $\text{GdAlO}_3$ ,  $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{AlO}_{3-\delta}$ ).
3. Synthesis and investigation of strontium substituted perovskite structure lanthanum cobaltates ( $\text{LaCoO}_3$ ,  $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ ).
4. Synthesis and investigation of strontium substituted perovskite structure gadolinium cobaltates ( $\text{GdCoO}_3$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ ).
5. Investigation of influence of starting materials, synthesis temperature, complexing agents and other parameters on the sinterability and phase purity of the end ceramics ( $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ).

**Statements for defence:**

- 1) Simple and effective sol-gel synthesis method is suitable for the preparation of monophasic perovskite structure gadolinium aluminate ( $\text{GdAlO}_3$ ), lanthanum and gadolinium cobaltates ( $\text{LaCoO}_3$ ,  $\text{GdCoO}_3$ ).
- 2) Sol-gel synthesis method can be used for the preparation of strontium substituted gadolinium aluminates ( $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{AlO}_{3-\delta}$ ,  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{AlO}_{3-\delta}$ ), lanthanum and gadolinium cobaltates ( $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ ,

$\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ ,  
 $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ ).

- 3) There was investigated influence of different synthesis parameters on the phase purity and crystallinity of the end ceramics. For the preparation of  $\text{GdAlO}_3$ ,  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$  ceramics the  $\text{Gd}_2\text{O}_3$  instead of  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  preferably should be used as starting material. Synthesis temperature, the amount of substituent, nature of complexing agent influences the phase purity and crystallinity of  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ,  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  products.

## 2. EXPERIMENTAL

### 2.1. Materials and reagents

For the sol-gel synthesis stoichiometric amounts of  $\text{Gd}_2\text{O}_3$ ,  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Sr}(\text{CH}_3\text{COO})_2$ ,  $\text{La}(\text{NO}_3)_3$ ,  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  as starting compounds, 1,2-ethanediol, natural and synthetic tartaric acids, citric acid, ethanolamine and EDTA as complexing agents, all of them analytical grade, were used. For the preparation different solutions the initials salts or oxides were dissolved in 0.2 mol/l acetic acid or distilled water.

### 2.2. Methods of analysis and synthesis

Gadolinium aluminate  $\text{GdAlO}_3$  and gadolinium-strontium aluminates  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$  ceramic samples synthesized by an aqueous sol-gel processing route. There were taken stoichiometric amounts of starting materials for the Gd–Al–O and Gd(Sr)–Al–O gels preparation. The gels were prepared using stoichiometric amounts of analytical grade  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Gd}_2\text{O}_3$  as  $\text{Gd}^{3+}$  raw materials,  $\text{Sr}(\text{NO}_3)_2$  as  $\text{Sr}^{2+}$  source and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as  $\text{Al}^{3+}$  source.

For the preparation of nonsubstituted  $\text{GdAlO}_3$  samples, gadolinium nitrate or gadolinium oxide respectively was first dissolved in 50 mL of 0.2 mol/L  $\text{CH}_3\text{COOH}$  at 65 °C. To this solution, aluminium nitrate 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  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$  ( $x = 0.00, 0.10, 0.25, 0.50$  and  $0.75$ ) samples the appropriate amount of strontium nitrate dissolved in 50 mL of 0.2 mol/L  $\text{CH}_3\text{COOH}$  at 65 °C was added and the resulting mixtures were stirred for 1 h at the same temperature.

In a following step, one of complexing agents (1,2-ethanediol, natural and synthetic tartaric acids, citric acid, ethanolamine) or there mixtures was added to the reaction solution. After concentrating the solutions by a slow evaporation at 65 °C under stirring, the Gd–Al–O or

Gd(Sr)–Al–O sols turned into white transparent gels. The oven dried (100 °C) gel powders were ground in an agate mortar and preheated for 3 h at 800 °C in air. Since the gels are very combustible, a slow heating rate ( $\sim 3\text{--}4\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ) especially between 100 and 400 °C was found to be essential. After an intermediate grinding in an agate mortar, the powders were additionally sintered in air for 10 h at 1000 °C and at 800 °C (for  $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$  ir  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  samples).

Lanthanum cobaltate  $\text{LaCoO}_3$  and lanthanum–strontium cobaltate  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  and  $0.75$ ), gadolinium cobaltate  $\text{GdCoO}_3$  and gadolinium–strontium cobaltate  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  and  $0.75$ ) ceramic samples were synthesized by an aqueous sol-gel method. The gels were prepared using stoichiometric amounts of analytical-grade lanthanum nitrate  $\text{La}(\text{NO}_3)_3$  or gadolinium oxide  $\text{Gd}_2\text{O}_3$ , strontium nitrate  $\text{Sr}(\text{NO}_3)_2$  and cobalt acetate tetrahydrate  $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ . For the preparation of unsubstituted samples by the sol-gel process, lanthanum nitrate or gadolinium oxide was first dissolved in 50 mL of 0.2 mol/L  $\text{CH}_3\text{COOH}$  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 ( $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  or  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ,  $x = 0.25, 0.50$  and  $0.75$ ) samples the appropriate amount of strontium nitrate dissolved in 50 mL of 0.2 mol/L  $\text{CH}_3\text{COOH}$  at 65 °C was added and the resulting mixtures were stirred for 1 h at the same temperature. In a following step, one of complexing agents (1.2-ethanediol, EDTA, natural tartaric or citric acid) was added to the reaction solution. After concentrating the solutions by a slow evaporation at 65 °C under stirring, the La–Co–O, La(Sr)–Co–O and Gd–Co–O, Gd(Sr)–Co–O 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.

### 2.3. Characterization and techniques

The thermal decomposition processes of the precursor gels were studied in air atmosphere by thermogravimetric, differential thermal and differential scanning calorimetry analyses (TG, DTA and DSC, respectively) using a Setaram TG-DSC12 (for  $\text{GdAlO}_3$ ,  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$ ), Netzsch STA 409 (for  $\text{LaCoO}_3$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ) and Netzsch STA 449 C (for  $\text{GdCoO}_3$ ,  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ) apparatuses at a heating rate  $5\text{--}10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . The infrared spectra in the range of  $4000\text{--}400\text{ cm}^{-1}$  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 Stoe-Cie Powder Diffraction System STADI P (CuK $\alpha$  radiation) (for GdAlO $_3$ , Gd $_{1-x}$ Sr $_x$ AlO $_{3-\delta}$ ), Stoe-Cie Powder Diffraction System STADI P diffractometer (MoK $\alpha$  radiation) (for GdAlO $_3$ , when complexing agent – 1.2-ethanediol, natural and synthetic tartaric acids, citric acid, ethanolamine or there mixtures), Siemens D5000 (CuK $\alpha$  radiation) (for LaCoO $_3$ , La $_{1-x}$ Sr $_x$ CoO $_{3-\delta}$ , GdCoO $_3$ , Gd $_{1-x}$ Sr $_x$ CoO $_{3-\delta}$ ) diffractometers. Scanning electron microscopy (SEM) was used to study the morphology of the samples. The SEM analysis was performed under vacuum in the specimen chamber of scanning electron microscope CAMECA SX 100 (for GdAlO $_3$ , when complexing agent – 1.2-ethanediol), DSM 962 (for GdAlO $_3$ , Gd $_{1-x}$ Sr $_x$ AlO $_{3-\delta}$ ), JEOL JSM 6400 (for LaCoO $_3$ , La $_{1-x}$ Sr $_x$ CoO $_{3-\delta}$ ), FEI NOVA nanoSEM 600 (for GdCoO $_3$ , Gd $_{1-x}$ Sr $_x$ CoO $_{3-\delta}$ ).

### 3. RESULTS AND DISCUSSION

#### 3.1. Sol-gel synthesis of perovskite structure GdAlO $_3$ and Gd $_{1-x}$ Sr $_x$ AlO $_{3-\delta}$

The synthesis of GdAlO $_3$  and Gd $_{1-x}$ Sr $_x$ AlO $_{3-\delta}$  via simple aqueous sol–gel method has been suggested. Systematic studies have been reported on influence of different synthesis parameters, such as starting materials and complexing agents, on the purity of GdAlO $_3$  and Gd $_{1-x}$ Sr $_x$ AlO $_{3-\delta}$  for the first time.

##### 3.1.1. Influence of starting materials on the purity of GdAlO $_3$ ceramics

The main objective of the present study is to synthesize perovskite GdAlO $_3$  via simple aqueous sol–gel method using different gadolinium starting materials. Also, we report here on the characterization of phases formed during various stages of sol–gel processing. Results, using these starting materials – Gd(NO $_3$ ) $_3$ ·6H $_2$ O and Gd $_2$ O $_3$  as Gd $^{3+}$  raw materials, Al(NO $_3$ ) $_3$ ·9H $_2$ O as Al $^{3+}$  source, are reported in this part. Complexing agent 1.2-ethanediol was taken.

##### 3.1.1.1. Characterization of Gd–Al–O gels

The IR spectra of two gels prepared using different raw materials are shown in Fig. 1. Clearly, both IR spectra qualitatively are identical regardless of used synthetic procedure. A broad absorption in the spectra of the precursor gels at around 3300–3400 cm $^{-1}$  indicates the presence of adsorbed water. In the 850–400 cm $^{-1}$  region of the IR spectra the observed specific peaks may be attributed to the characteristic M–O vibrations (probably, Gd–O, Al–O). The absorptions at ca. 3100–2800 cm $^{-1}$  and 1430–1410 cm $^{-1}$  are due to stretch vibrations in –CH $_3$  and >CH $_2$ ; strong bands at 3400–3200 cm $^{-1}$  and 1100–1000 cm $^{-1}$ , and medium bands at 1300–1200 cm $^{-1}$  are probably due to –CH $_2$ –OH stretching; the strong bands due to –CO–OH stretching can be identified at 3500–3200 cm $^{-1}$ , 1700–1550 cm $^{-1}$  and 1350–1340 cm $^{-1}$ , as well as at the medium bands at 950–800 cm $^{-1}$ . The characteristic nitrate stretching frequencies at

1700–1600  $\text{cm}^{-1}$  might be overlapped with the  $-\text{CO}-\text{OH}$  stretching. According to the IR results we suppose that all three ligands (acetate, nitrate and glycolate) are in the coordination sphere of the metals. Consequently, the conclusion can be made that the gels obtained are individual compounds but not physical mixtures of starting materials.

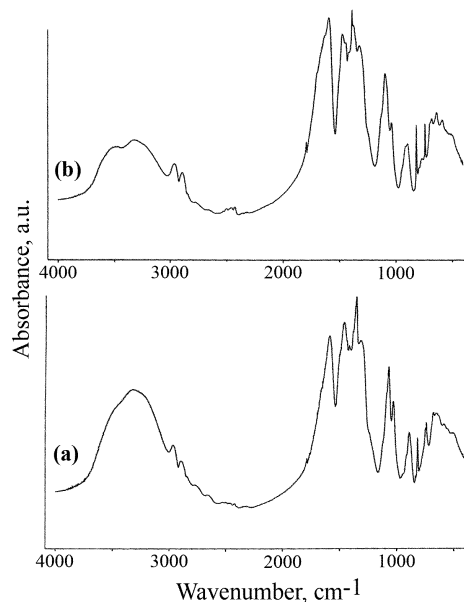


Fig. 1. Infrared spectra of the Gd-Al-O precursor gels prepared using different raw materials in the sol-gel processing: (a) gadolinium nitrate and (b) gadolinium oxide.

The XRD patterns of the Gd-Al-O acetate-nitrate-glycolate dried gels (Fig. 2) mostly showed broad peaks due to the amorphous character of the powders. No peaks due to insignificant crystallization of metal acetates, glycolates, or nitrates, or crystallization of any undesired or contaminating phase could be identified in the XRD pattern of sample, prepared using gadolinium oxide (see Fig. 2b). However, the XRD pattern of precursor gel prepared using gadolinium nitrate as starting material shows very few low intensity diffraction lines at around  $2\theta$  of  $36.8^\circ$ ,  $42.4-44.0^\circ$  and  $57.8^\circ$ . Thus, the XRD analysis data show that this sample is not individual compound, since partial crystallization of initial salt of gadolinium takes place during gelation. Therefore, we can conclude that the conditions of the sol-gel preparation using gadolinium nitrate as starting material are not fully optimized. The XRD results show that homogeneity of two Gd-Al-O acetate-nitrate-glycolate gels prepared using gadolinium oxide and gadolinium nitrate as starting materials is slightly different. Could this feature affect the phase purity of the end ceramic material? This question will be answered in the next part of the work.

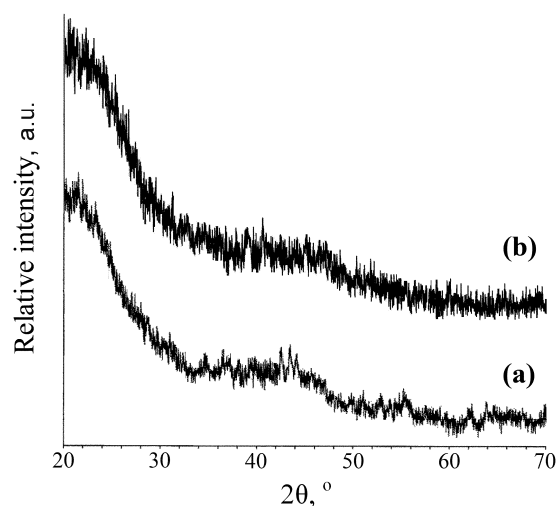


Fig. 2. X-ray diffraction patterns of the Gd–Al–O precursor gels prepared using different raw materials in the sol-gel processing: (a) gadolinium nitrate and (b) gadolinium oxide.

The mechanism of the thermal decomposition in flowing air of these two Gd–Al–O precursor gels was studied by TG/DTA measurements. Both TG curves show a three-step decomposition of the precursor to form the ceramic material. The temperature ranges of weight losses ( $\sim 20\text{--}175\text{ }^{\circ}\text{C}$ ,  $\sim 175\text{--}805\text{ }^{\circ}\text{C}$  and  $\sim 805\text{--}1000\text{ }^{\circ}\text{C}$ ) are very similar in these samples. The initial weight loss below  $175\text{ }^{\circ}\text{C}$  ( $\sim 5\text{--}6\%$ ) is due to the evaporation of water and solvent molecules as indicated by minor endotherms on the DTA curves in this region. The second and most significant decomposition step can be attributed to the pyrolysis and combustion of organic compounds and the degradation of intermediate species formed during the gelation process. This observation is corroborated by well-resolved exotherm in the DTA curves at approximately  $400\text{--}500\text{ }^{\circ}\text{C}$ . The final weight loss ( $\sim 2.5\text{--}4.8\%$ ) on the TG curves of the gel samples was observed in the temperature range of  $805\text{--}1000\text{ }^{\circ}\text{C}$ . The thermal decomposition behaviour is associated with weak exothermic effects in the DTA curves. These peaks probably correspond to the decomposition of the intermediate oxycarbonates  $\text{Gd}_2\text{O}_2\text{CO}_3$  or  $\text{Al}_2\text{O}_2\text{CO}_3$  to the oxides. According to the thermal analysis data the crystallization of  $\text{GdAlO}_3$  ceramic oxides could vary from  $900$  to  $1000\text{ }^{\circ}\text{C}$ . Therefore, the final annealing temperature of  $1000\text{ }^{\circ}\text{C}$  for the preparation of  $\text{GdAlO}_3$  phase was selected.

#### 3.1.1.2. Characterization of $\text{GdAlO}_3$ ceramic materials

The X-ray diffraction patterns for the products sintered for 10 h at  $1000\text{ }^{\circ}\text{C}$  are shown in Fig. 3. According to XRD analysis, sintering of Gd–Al–O precursor gel obtained from  $\text{Gd}_2\text{O}_3$  produced fully crystalline single-phase  $\text{GdAlO}_3$  ceramic. As seen from Fig. 3b, all diffraction peaks in this XRD spectrum could be attributed to the perovskite crystal structure of  $\text{GdAlO}_3$  (PDF [46–395]). However, in the case of gadolinium nitrate derived precursor, along with

perovskite gadolinium aluminate the formation of the impurity phases such as  $Gd_2O_3$  (PDF [43–1014]),  $Gd_3Al_5O_{12}$  (PDF [32–383]) and  $Gd_4Al_2O_9$  (PDF [46–396]) is evident (see Fig. 3a).

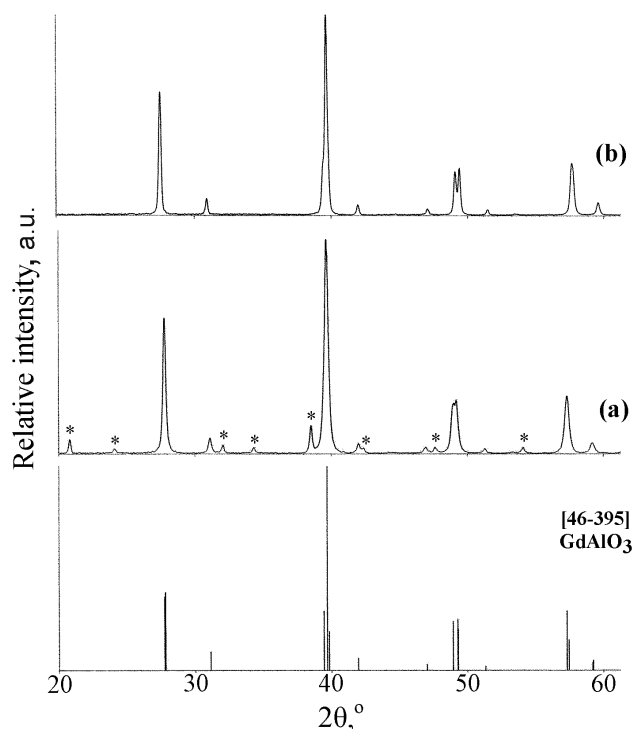


Fig. 3. X-ray diffraction patterns of  $GdAlO_3$  ceramics prepared using different raw materials in the sol-gel processing: (a) gadolinium nitrate and (b) gadolinium oxide. Schematic presentation of the XRD pattern of  $GdAlO_3$  from JCPDS is presented at the bottom. The impurity phases are marked.

Fig. 4 shows the SEM micrographs (back scattered electron (BSE) images) of synthesized  $GdAlO_3$  powders using gadolinium nitrate and gadolinium oxide in the initial stage of preparation. As was expected, in the backscattered electron mode for the  $GdAlO_3$  sample prepared using gadolinium nitrate numerous light and dark regions are observed. Since the brightness of the specimen is highly inhomogeneous over the entire measuring area, evidently the material is composed of several phases. The SEM image of the single-phase  $GdAlO_3$  sample confirms that the most of the material is finely divided, i.e. the distribution of its chemical elements is highly uniform. As seen, the broad distribution of light or dark regions the SEM image (Fig. 4, top) is absent. Some individual particles seem to be nano-sized plate-like crystals, however, the most grains are agglomerated having different size which ranges from  $\sim 5$ – $30 \mu m$ .

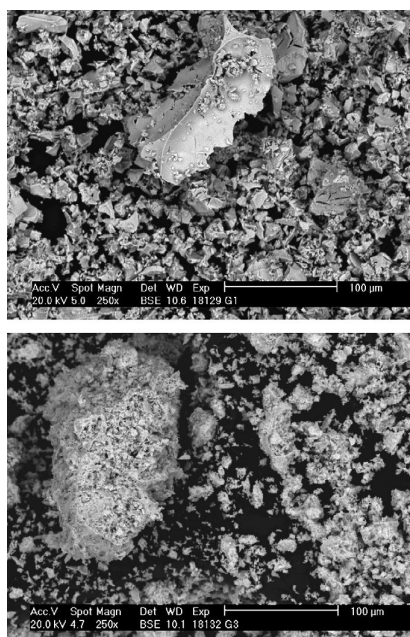


Fig. 4. Scanning electron micrographs in back scattering mode of  $GdAlO_3$  ceramics prepared using different raw materials in the sol-gel processing: (at bottom) gadolinium nitrate and (at top) gadolinium oxide.

The reported results let us to conclude that the developed aqueous sol-gel procedure could be successfully used for the low-temperature synthesis of monophasic perovskite gadolinium aluminate ceramics. It was also demonstrated that the selection of raw materials for the sol-gel processing should be done with care. The proposed sol-gel method of preparation of  $GdAlO_3$  in aqueous media is inexpensive, environmentally friendly and thus appropriate for the large scale production of such type ceramics.

### 3.1.2. Synthesis of $GdAlO_3$ using different complexing agents

This part presents on the results of the sol-gel preparation of the microcrystalline gadolinium aluminate ( $GdAlO_3$ ) ceramics at slightly different synthetic conditions. Metal ions generated by dissolving the starting materials of metals in the diluted acetic acid were complexed by different complexing agents (natural and synthetic tartaric acids, 1,2-ethanediol, citric acid, ethanolamine) to obtain the precursors for the  $GdAlO_3$ .

The X-ray diffraction patterns of the  $GdAlO_3$  ceramics prepared using gadolinium oxide as a gadolinium source and the same complexing agents (natural and synthetic tartaric acids) are shown in Fig. 5.

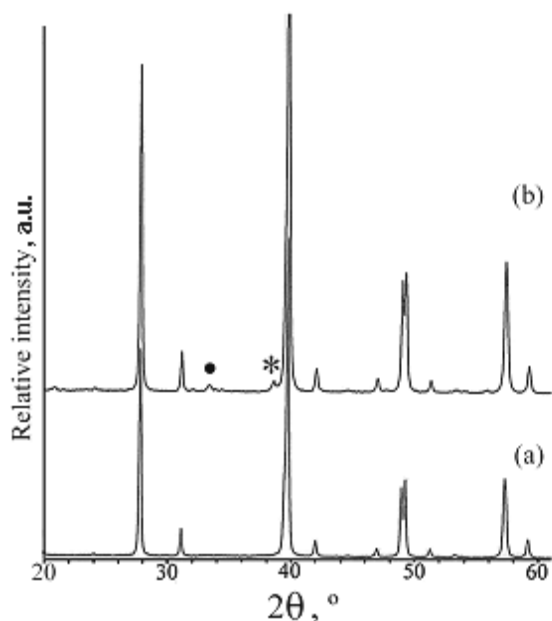


Fig. 5. X-ray diffraction patterns of a  $\text{GdAlO}_3$  ceramic sample prepared using gadolinium oxide as a gadolinium source and natural tartaric acid (a) or synthetic tartaric acid (b) as complexing agents in the sol-gel processing. The impurity phases are marked: \* –  $\text{Gd}_3\text{Al}_5\text{O}_{12}$ , • –  $\text{Gd}_2\text{O}_3$ .

According to the XRD analysis, sintering of the Gd–Al–O precursor gel obtained using  $\text{Gd}_2\text{O}_3$  as a starting material and natural tartaric acid as a complexing agent, produced fully crystalline single-phase  $\text{GdAlO}_3$  ceramics. As it can be seen from Fig. 5a, all diffraction peaks in this XRD spectrum could be attributed to the perovskite crystal structure of  $\text{GdAlO}_3$  (PDF [46–395]). However, in the case when synthetic tartaric acid was used as a complexing agent, along with perovskite gadolinium aluminate the formation of the impurity phases such as  $\text{Gd}_2\text{O}_3$  (PDF [43–1014]) and  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  (PDF [32–383]) is evident (see Fig. 5b).

The X–ray diffraction patterns of the  $\text{GdAlO}_3$  ceramics prepared using 1.2-ethanediol, citric acid and a mixture of citric acid and ethanolamine as complexing agents in the sol-gel processing are shown in Fig. 6. According to the XRD analysis, all three diffraction patterns show the formation of fully crystalline single-phase  $\text{GdAlO}_3$  ceramic samples. All diffraction lines in these XRD spectra could be attributed to the  $\text{GdAlO}_3$  phase having a perovskite crystal structure (PDF [46-395]). Thus, we can conclude that the three complexing agents (natural tartaric acid, 1.2-ethanediol and citric acid) as well as the mixture of citric acid and ethanolamine are suitable complexing reagents for the sol-gel preparation of  $\text{GdAlO}_3$ .

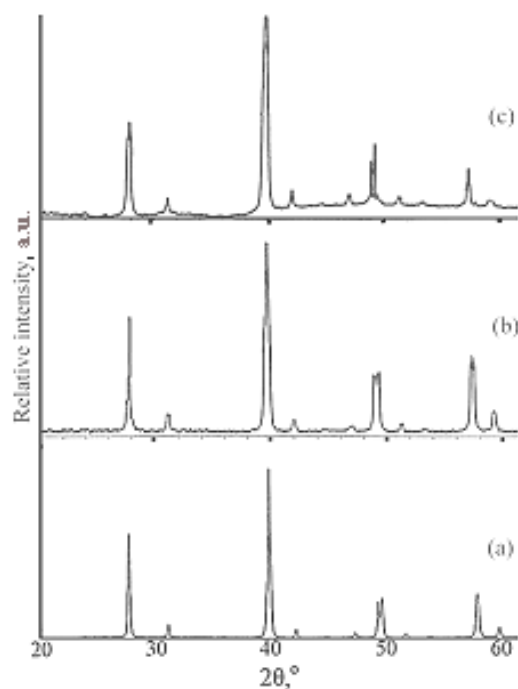


Fig. 6. X-ray diffraction patterns of a  $\text{GdAlO}_3$  ceramic sample prepared using gadolinium oxide as gadolinium source and 1,2-ethanediol (a), citric acid (b), or a mixture of citric acid and ethanolamine (c) as complexing agents in the sol-gel processing.

The most interesting results were obtained when we used double mixtures of natural tartaric acid and 1,2-ethanediol or citric acid and 1,2-ethanediol in the sol-gel process. It turned out that the use of double mixtures of the complexing agents gave the opposite results. In the case of the mixture of natural tartaric acid and 1,2-ethanediol, the diffraction lines at  $2\theta = 21.8^\circ$ ,  $33.7^\circ$  and  $35.4^\circ$  could be attributed to the  $\text{Gd}_4\text{Al}_2\text{O}_9$  phase. When the mixture of citric acid and 1,2-ethanediol was used in the sol-gel synthesis, the main phase determined was  $\text{Gd}_4\text{Al}_2\text{O}_9$ , and the side phases were  $\text{GdAlO}_3$ ,  $\text{Gd}_2\text{O}_3$  and  $\text{Gd}_3\text{Al}_5\text{O}_{12}$ . So, the question why individual complexing agents are suitable for the sol-gel preparation of a single phase  $\text{GdAlO}_3$ , while their double mixtures cannot be successfully used, is still pending.

The textural properties of the same calcined powders were investigated by SEM, from which the grain size and typical morphologies were obtained.

From the present study it could be concluded that the formation of perovskite  $\text{GdAlO}_3$  ceramics during the sol-gel synthesis depends on the nature of the starting materials and complexing agents. The monophasic  $\text{GdAlO}_3$  was obtained when gadolinium oxide as a gadolinium source and natural tartaric acid, 1,2-ethanediol, citric acid or mixture of citric acid and ethanolamine as complexing agents were used in the sol-gel processing.

### 3.1.3. Influence of starting materials to the purity of $Gd_{1-x}Sr_xAlO_{3-\delta}$ ceramics

This part reports on the results concerning the sol-gel preparation of the nanocrystalline nonsubstituted and Sr-substituted gadolinium aluminate ceramics at slightly different synthetic conditions. The metal ions, generated by dissolving starting materials of metals in the diluted acetic acid were complexed by 1.2-ethanediol to obtain the precursors for the nonsubstituted and Sr-substituted  $GdAlO_3$ . In the sol-gel processing different starting gadolinium materials such as gadolinium nitrate or gadolinium oxide were employed. The influence of the synthesis temperature and the amount of substituent on the phase purity of  $GdAlO_3$  was also investigated.

#### 3.1.3.1. Characterization of $Gd_{1-x}Sr_xAlO_{3-\delta}$ gels

The mechanism of the thermal decomposition in flowing air of Gd(Sr)-Al-O precursor gels was studied by TG/DTA measurements. The TG/DTA profiles for the precursor gels  $GdAlO_3$ ,  $Gd_{0.90}Sr_{0.10}AlO_{3-\delta}$  and  $Gd_{0.75}Sr_{0.25}AlO_{3-\delta}$ , prepared using gadolinium nitrate as  $Gd^{3+}$  source, are shown in Fig. 7. According to the thermal analysis data the crystallisation of  $Gd_{1-x}Sr_xAlO_{3-\delta}$  ceramic oxides could vary from 800 to 1000 °C. Therefore, the final annealing temperature of 1000 °C for the preparation of gadolinium aluminate was selected.

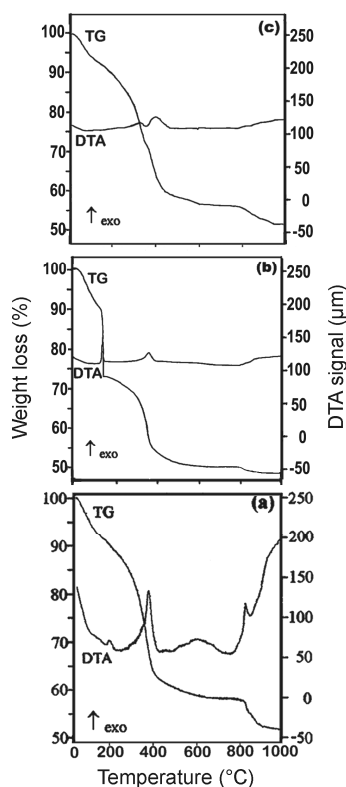


Fig. 7. TG and DTA profiles of the Gd(Sr)-Al-O precursor gels (a – 0% Sr, b – 10% Sr, c – 25% Sr) prepared using gadolinium nitrate in the sol-gel processing. The heating rate was  $5\text{ }^{\circ}\text{C min}^{-1}$ .



### 3.1.3.2. Characterization of $Gd_{1-x}Sr_xAlO_{3-\delta}$ ceramics

The Gd(Sr)-Al-O precursor gel powders prepared using gadolinium nitrate in the sol-gel processing were calcined and sintered at 1000 °C. The XRD patterns of  $Gd_{0.90}Sr_{0.10}AlO_{3-\delta}$ ,  $Gd_{0.75}Sr_{0.25}AlO_{3-\delta}$ ,  $Gd_{0.50}Sr_{0.50}AlO_{3-\delta}$  and  $Gd_{0.25}Sr_{0.75}AlO_{3-\delta}$  ceramics are shown in Fig. 8. According to the XRD analysis, fully crystallized single-phase oxide  $GdAlO_3$  with well pronounced perovskite crystal structure has formed (see Fig. 8a) (PDF [46-395]). The XRD pattern of the sample with 10% of strontium is presented in Fig. 8b. The XRD data confirm  $Gd_{0.90}Sr_{0.10}AlO_{3-\delta}$  to be the main crystalline component. However the formation of certain amount of the impurity phases already was detected. Figure 9c shows the X-ray diffraction pattern of the ceramic sample with nominal composition of  $Gd_{0.75}Sr_{0.25}AlO_{3-\delta}$ . The diffraction lines assignable to the perovskite crystal structure at  $2\theta \approx 27.5^\circ$ ,  $31.1^\circ$ ,  $39.2^\circ$ ,  $42.1^\circ$ ,  $46.9^\circ$ ,  $49.0^\circ$ ,  $51.3^\circ$ ,  $57.4^\circ$  and  $59.3^\circ$  are well pronounced in the diffractogram. However, the intensities of diffraction lines attributable to the impurity phases such as  $Gd_4Al_2O_9$ ,  $Gd_3Al_5O_{12}$  and  $Sr_3Al_2O_6$  are much higher than was observed for the previous sample. With further increasing the Sr content, the formation of perovskite aluminate seems to be problematic. The impurity phases ( $SrGdAlO_4$  and  $SrAl_2O_4$ ) already are the dominating component formed during the synthesis of  $Gd_{0.25}Sr_{0.75}AlO_{3-\delta}$  ceramics (Fig. 8e).

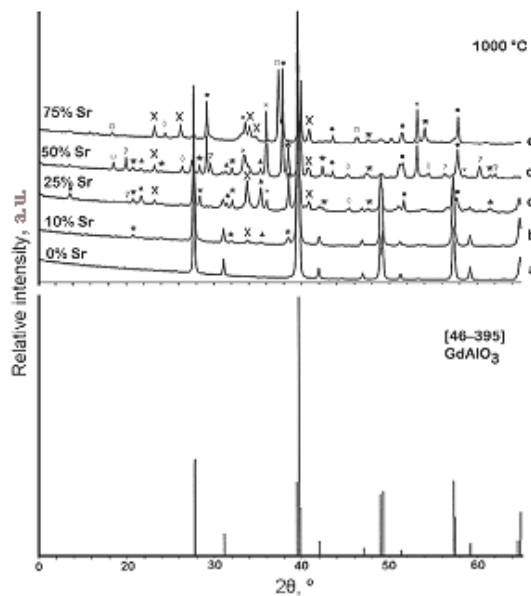


Fig. 8. X-ray diffraction patterns of: (a)  $GdAlO_3$ , (b)  $Gd_{0.90}Sr_{0.10}AlO_{3-\delta}$ , (c)  $Gd_{0.75}Sr_{0.25}AlO_{3-\delta}$ , (d)  $Gd_{0.50}Sr_{0.50}AlO_{3-\delta}$ , (e)  $Gd_{0.25}Sr_{0.75}AlO_{3-\delta}$  ceramics prepared using gadolinium nitrate in the sol-gel processing. Schematic presentation of the XRD pattern of  $GdAlO_3$  from JCPDS is presented at the bottom. The impurity phases are marked:  $\times$  –  $SrAl_4O_7$ ,  $\blacktriangle$  –  $Gd_4Al_2O_9$ ,  $\diamond$  –  $Sr_4Al_2O_7$ ,  $X$  –  $SrAl_2O_4$ ,  $*$  –  $Gd_3Al_5O_{12}$ ,  $\square$  –  $Sr_3Al_2O_6$ ,  $\bullet$  –  $SrGdAlO_4$ ,  $?$  – unidentified phases.

As was mentioned, one of the goals of this study was to investigate the influence of nature of starting material used as gadolinium source on the sinterability and phase purity of the end ceramics. Again, according to the XRD analysis the synthesized at 1000 °C non-substituted compound was a single-phase gadolinium aluminate ( $\text{GdAlO}_3$ ). Next, the influence of sintering temperature on the quality of Sr-substituted gadolinium aluminates was also estimated. The X-ray diffraction patterns of the  $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$  ceramics prepared using gadolinium oxide in the sol-gel processing and annealed at different temperatures are shown in Fig. 9. As seen, lot of different impurity phases in the X-ray diffraction pattern of the sample annealed at 800 °C could be detected (see Fig. 9a). Apparently, this synthesis temperature is too low for the preparation of monophasic perovskite phase. The diffraction lines assignable to the perovskite crystal structure are well pronounced in the X-ray diffraction pattern of the sample annealed at higher temperature (1000 °C; see Fig. 9b).

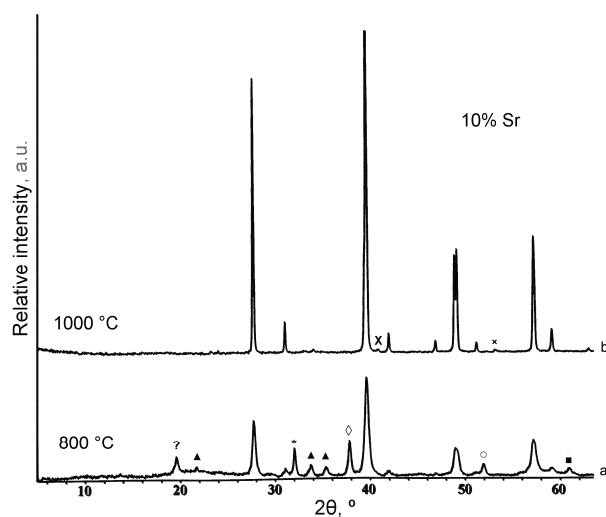


Fig. 9. X-ray diffraction patterns of  $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$  ceramics prepared using gadolinium oxide in the sol-gel processing at different temperature: (a) 800 °C, (b) 1000 °C. The impurity phases are marked: × –  $\text{SrAl}_4\text{O}_7$ , ▲ –  $\text{Gd}_4\text{Al}_2\text{O}_9$ , ◇ –  $\text{Sr}_4\text{Al}_2\text{O}_7$ , X –  $\text{SrAl}_2\text{O}_4$ , \* –  $\text{Gd}_3\text{Al}_5\text{O}_{12}$ , ○ –  $\text{SrGd}_2\text{O}_4$ , ■ –  $\text{GdAl}_{11}\text{O}_{18}$ , ? – unidentified phases.

The X-ray diffraction patterns of the  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  ceramics prepared using gadolinium oxide in the sol-gel processing at different temperatures confirmed once again that the final annealing temperature should be higher than 800 °C. Moreover, with increasing the strontium concentration the amount of impurity phases in the sample annealed at 1000 °C also increases. However it is evident that using the  $\text{Gd}_2\text{O}_3$  as starting material in the sol-gel processing the obtained gadolinium aluminate perovskite phase ceramics contain less amount of impurities than that using the gadolinium nitrate.

So we can conclude that for the preparation of  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  ceramics the gadolinium oxide instead of gadolinium nitrate preferably should be used as starting material.

The obtained X-ray diffraction results are mainly consistent with the crystallization process observed by the IR measurements.

Fig. 10 shows the SEM micrographs (back scattered electron (BSE) images) of synthesized  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  powders using gadolinium oxide in the initial stage of preparation.

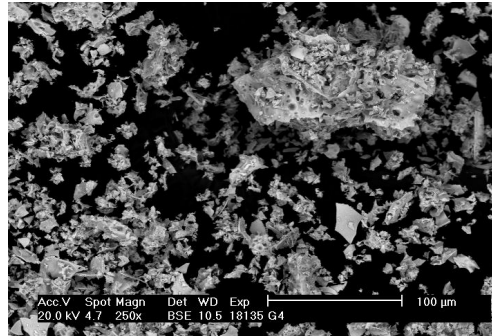


Fig. 10. Scanning electron micrographs in back scattering mode of  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  ceramics prepared using gadolinium oxide in the sol-gel processing.

In the backscattered electron mode for the  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  sample prepared using gadolinium oxide numerous light and dark regions are observed. Since the brightness of the specimen is highly inhomogeneous over the entire measuring area, evidently the material is composed of several phases.

#### **3.1.4. Synthesis of $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$ using different complexing agents**

This part presents on the results of the sol-gel preparation of the microcrystalline  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$  ( $x = 0.10, 0.25$ ) ceramics, prepared using gadolinium oxide as  $\text{Gd}^{3+}$  raw material. Metal ions were complexed by different complexing agents (natural tartaric acid or EDTA). The  $\text{Gd}(\text{Sr})\text{-Al-O}$  precursor gel powders prepared using natural tartaric acid as complexing agents in the sol-gel process were calcined and sintered at  $1000^\circ\text{C}$ . The XRD patterns of the obtained ceramics contain diffraction lines which could be attributed to the phase of perovskite structure  $\text{GdAlO}_3$ . There can be seen such impurity phases –  $\text{Gd}_3\text{Al}_5\text{O}_{12}$  ( $2\theta \approx 20.8^\circ, 24.1^\circ, 42.5^\circ$ ),  $\text{Gd}_4\text{Al}_2\text{O}_9$  ( $2\theta \approx 13.6^\circ, 21.7^\circ, 33.9^\circ, 35.1^\circ, 40.9^\circ, 45.3^\circ$ ),  $\text{Gd}_2\text{O}_3$  ( $2\theta \approx 23.4^\circ, 33.3^\circ, 38.6^\circ, 45.7^\circ, 49.9^\circ, 53.9^\circ, 55.8^\circ, 61.3^\circ$ ),  $\text{Sr}_4\text{Al}_2\text{O}_7$  ( $2\theta \approx 36.2^\circ, 38.0^\circ$ ) and unidentified ( $2\theta \approx 18.6^\circ, 20.1^\circ, 26.4^\circ, 29.7^\circ, 43.0^\circ, 47.4^\circ, 51.2^\circ, 54.5^\circ, 56.6^\circ, 58.1^\circ, 60.3^\circ$ ), with 10% strontium in the sample. In case of  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  XRD data shows more impurity phases.

The Gd(Sr)–Al–O precursor gel powders prepared using EDTA as complexing agents also were sintered at 1000 °C. The XRD patterns of the obtained ceramics are shown in Fig. 11.

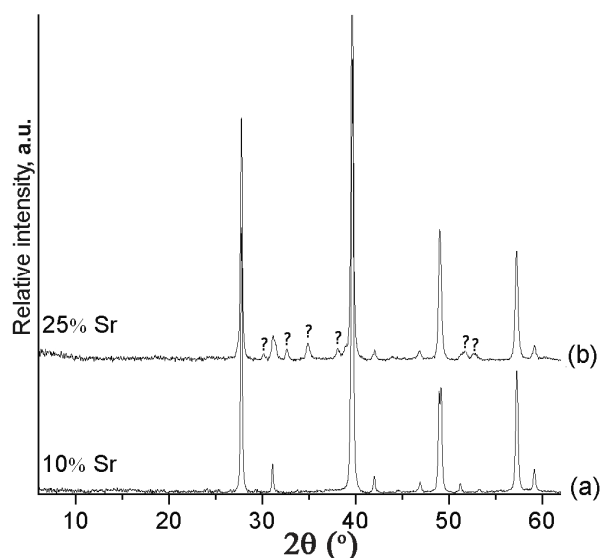


Fig. 11. X-ray diffraction patterns of  $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$  (a) or  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  (b) ceramics, prepared using EDTA as complexing agent and heated at 1000 °C in the sol-gel processing. The impurity phases are marked: ? – unidentified.

All diffraction lines in Fig. 11a are attributed to the perovskite structure  $\text{GdAlO}_3$  (PDF [46–395]). In the sample, prepared using EDTA as complexing agent, with 10% strontium formed single-phase gadolinium aluminate. The XRD data confirm  $\text{GdAlO}_3$  to be the main crystalline component in the  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{AlO}_{3-\delta}$  (see Fig. 11b). However the formation of certain amount of the impurity phases (unidentified at  $2\theta \approx 30.1^\circ, 32.6^\circ, 34.8^\circ, 38.0^\circ, 51.8^\circ, 52.8^\circ$ ) also was detected. It is evident that the samples, prepared using EDTA as complexing agent and with little amount of strontium, have no impurities or there are less than using natural tartaric acid.

### 3.2. Sol-gel synthesis of perovskite structure $\text{LaCoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$

There will be suggested the synthesis of  $\text{LaCoO}_3$  and  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  via simple aqueous sol-gel method. Gels were prepared using lanthanum nitrate, strontium nitrate, cobalt acetate tetrahydrate as starting materials, complexing agent – 1,2-ethanediol.

#### 3.2.1. Characterization of $\text{LaCoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ gels

The TG/DTA profiles for the precursor gels are shown in Fig. 12. TG curves showed that in all cases the thermal decomposition proceeded in a similar way.

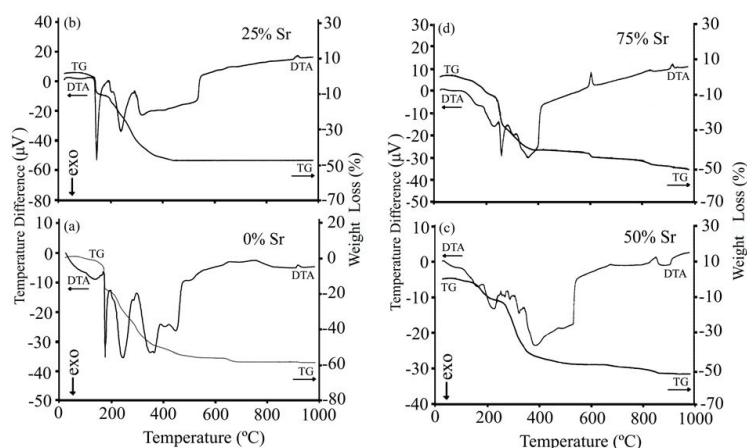


Fig. 12. TG and DTA profiles of (a) La-Co-O, (b) La(0.75)-Sr(0.25)-Co-O, (c) La(0.50)-Sr(0.50)-Co-O, and (d) La(0.25)-Sr(0.75)-Co-O precursor gels. The heating rate was  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

According to the thermal analysis data, the crystallization of  $\text{LaCoO}_3$  and  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ceramic oxides could vary from 900 to 1000  $^{\circ}\text{C}$ . Therefore, the final annealing temperature of 1000  $^{\circ}\text{C}$  for the sol-gel preparation of lanthanum cobaltate could be selected.

Fig. 13 shows the SEM micrographs of oven dried La(Sr)-Co-O precursor gels. In La-Co-O sample the scanning electron micrograph indicates the formation of monolithic gel. Strontium substituted samples showed slightly agglomerated particles.

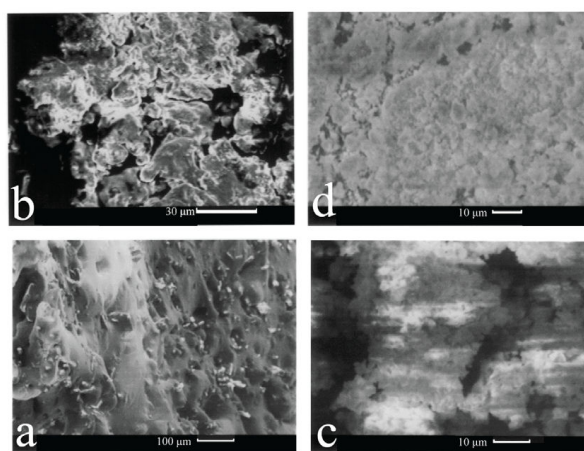


Fig. 13. Scanning electron micrographs of (a) La-Co-O, (b) La(0.75)-Sr(0.25)-Co-O, (c) La(0.50)-Sr(0.50)-Co-O, and (d) La(0.25)-Sr(0.75)-Co-O precursor gels.

### 3.2.2 Characterization of $\text{LaCoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ceramics

The XRD patterns of  $\text{LaCoO}_3$  ceramics heated at 500  $^{\circ}\text{C}$ , 700  $^{\circ}\text{C}$ , 900  $^{\circ}\text{C}$ , 1000  $^{\circ}\text{C}$  for 3 h and 10 h are shown in Figs. 14 and 15, respectively. According to the XRD analysis, a fully crystallized, almost single-phase oxide  $\text{LaCoO}_3$  with the well pronounced perovskite crystal structure has formed already after annealing the precursor for 3 h at 700  $^{\circ}\text{C}$  (see Fig. 14b) (PDF [48–123]). Impurity phases in the samples, attributable to  $\text{Co}_3\text{O}_4$  (diffraction lines at  $2\theta \approx 31.272, 36.853, 65.238$ ), and  $\text{La}_2\text{O}_3$  ( $2\theta \approx 29.961, 44.635$ ) however, also have been

detected. With prolonged annealing time (10 h) the monophasic lanthanum cobaltate has formed at 1000 °C (see Fig. 15).

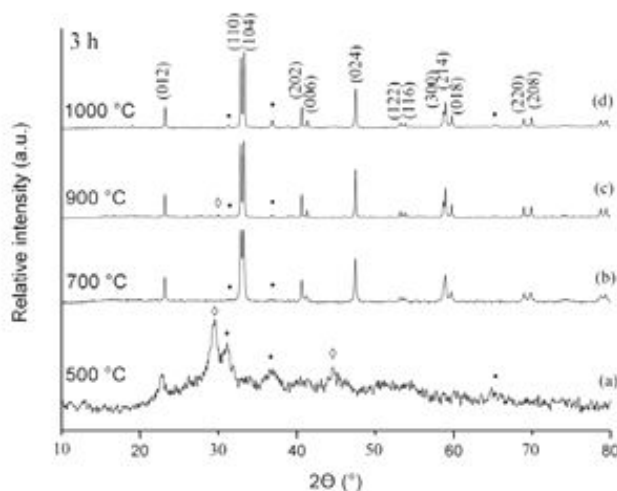


Fig. 14. X-ray diffraction patterns of LaCoO<sub>3</sub> ceramics synthesized using the sol-gel method at different temperatures: (a) 500 °C, (b) 700 °C, (c) 900 °C, (d) 1000 °C. Annealing time was 3 h. The Miller indices of LaCoO<sub>3</sub> phase are marked. Impurity phases: • - Co<sub>3</sub>O<sub>4</sub>, ◊ - La<sub>2</sub>O<sub>3</sub>.

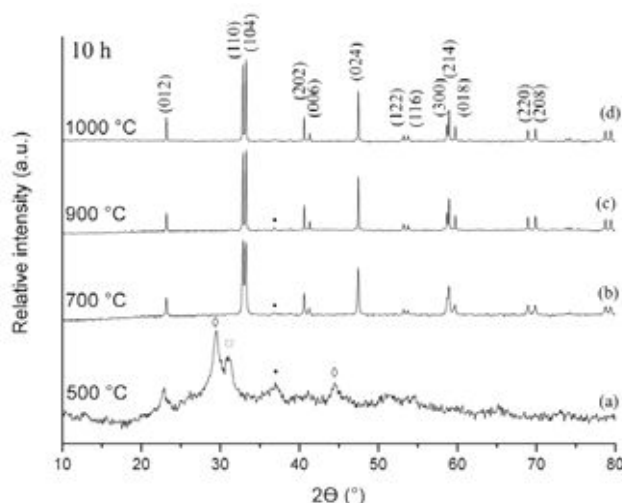


Fig. 15. X-ray diffraction patterns of LaCoO<sub>3</sub> ceramics synthesized using the sol-gel method at different temperatures: (a) 500 °C, (b) 700 °C, (c) 900 °C, (d) 1000 °C. Annealing time was 10 h. The Miller indices of LaCoO<sub>3</sub> phase are marked. Impurity phases: ◻ - Co<sub>2</sub>O<sub>3</sub>, • - Co<sub>3</sub>O<sub>4</sub>, ◊ - La<sub>2</sub>O<sub>3</sub>.

The XRD patterns of the strontium-substituted La<sub>0.75</sub>Sr<sub>0.25</sub>CoO<sub>3-δ</sub> sample heated at the same temperatures for 3 and 10 h are also performed. 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<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and SrCO<sub>3</sub>. The crystalline perovskite structure of strontium-substituted lanthanum cobaltate is obtained at higher temperature (900 °C). The XRD data clearly confirm LaCoO<sub>3</sub> to be the main crystalline component, independent of the annealing time. With further increasing strontium substitutional

level, the obtained X-ray diffraction results are very similar (Fig. 16). The formation of certain amounts of the impurity phases, such as  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{SrO}$ , is evident at lower temperatures. The main phase ( $\text{LaCoO}_3$ ) with perovskite crystal structure have formed at  $900^\circ\text{C}$ .

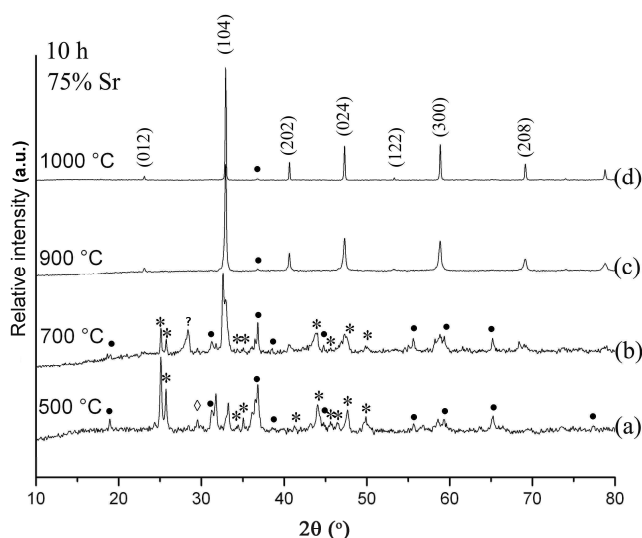


Fig. 16. X-ray diffraction patterns of  $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at different temperatures: (a)  $500^\circ\text{C}$ , (b)  $700^\circ\text{C}$ , (c)  $900^\circ\text{C}$ , (d)  $1000^\circ\text{C}$ . Annealing time was 10 h. The Miller indices of  $\text{LaCoO}_3$  phase are marked. Impurity phases: • –  $\text{Co}_3\text{O}_4$ , \* –  $\text{SrCO}_3$ , ◇ –  $\text{La}_2\text{O}_3$ , ? – unidentified phases.

This observation is opposite to the results obtained by investigating lanthanum and gadolinium 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  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  oxides.

Fig. 17 shows the SEM micrographs of  $\text{La}(\text{Sr})\text{-Co-O}$  gels heated at  $1000^\circ\text{C}$ . 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  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  solids synthesized by the sol-gel route are composed of irregular submicron grains with an average grain size of less than  $3\ \mu\text{m}$ .

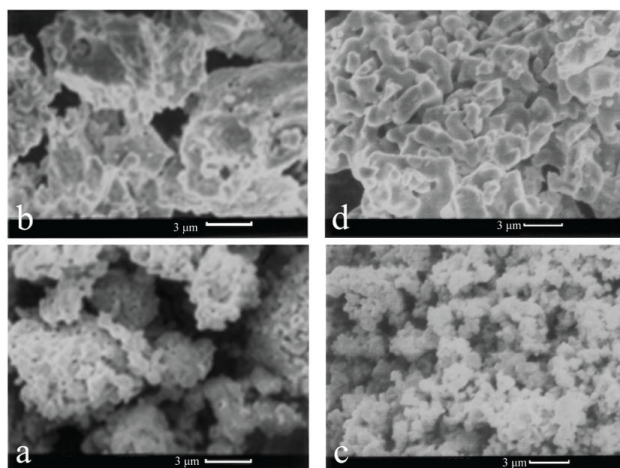


Fig. 17. Scanning electron micrographs of sol-gel derived (a)  $\text{LaCoO}_3$ , (b)  $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$  (d)  $\text{La}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics heated for 10 h at 1000 °C.

### 3.3. Sol-gel synthesis of perovskite structure $\text{GdCoO}_3$ and $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$

The synthesis of  $\text{GdCoO}_3$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  via simple aqueous sol-gel method has been suggested. Systematic studies have been reported on influence of different synthesis parameters, such as complexing agents, amount of strontium, synthesis temperature, for the purity of  $\text{GdCoO}_3$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  for the first time.

#### 3.3.1. Synthesis of $\text{GdCoO}_3$ and $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ using EDTA as complexing agent

This part reports on the results concerning the sol-gel preparation and characterization of  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  and  $0.75$ ). The metal ions, generated by dissolving starting materials in diluted acetic acid were complexed by EDTA to obtain the precursors for the non-substituted and Sr-substituted  $\text{GdCoO}_3$ .

The mechanism of the thermal decomposition in flowing air of  $\text{GdCoO}_3$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  and  $0.75$ ) precursor gels was studied by TG/DSC measurements. The TG/DSC profiles for these samples are shown in Fig. 18. The thermal decomposition behaviour is associated with weak exothermic effects in the DSC curves. According to the thermal analysis data the crystallisation of Gd(Sr)-Co-O ceramic oxides could vary from 700 to 1000 °C. Therefore, the final annealing temperature of 1000 °C for the preparation of perovskite phase was selected.



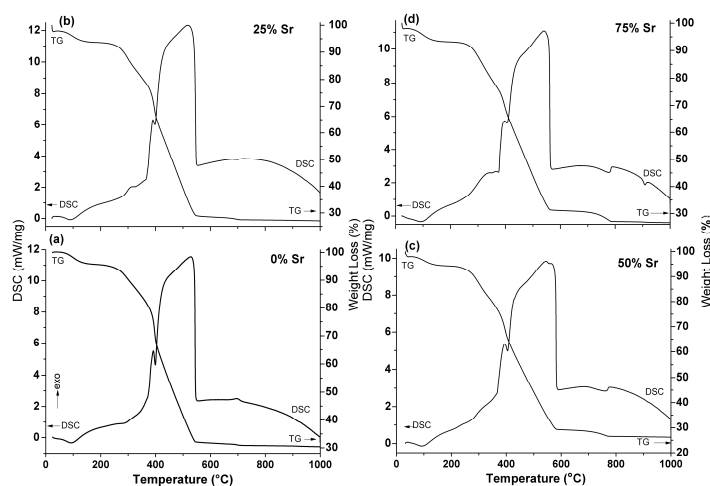


Fig. 18. TG and DSC profiles of the Gd(Sr)–Co–O precursor gels (a – 0% Sr, b – 25% Sr, c – 50% Sr, d – 75% Sr) in the sol-gel processing.

The XRD patterns of  $\text{GdCoO}_3$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  and  $0.75$ ) ceramics heated at 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C for 10 h are shown in Figs. 19, 20, 21, 22, 23 and 24, respectively.

According to the XRD analysis, the main phase  $\text{GdCoO}_3$  with the well pronounced perovskite crystal structure has formed already at 700 °C (see Fig. 19) (PDF [25–1057]). But there can be seen formation of other phases, such as  $\text{Gd}_2\text{O}_3$  ( $2\theta = 28.568, 53.581$ ),  $\text{SrCoO}_{2.52}$ , ( $2\theta = 28.531, 32.619, 43.872, 55.770, 58.195$ ) and unknown phases, when the Sr content is higher than 25% (see Fig. 19c and 19d).

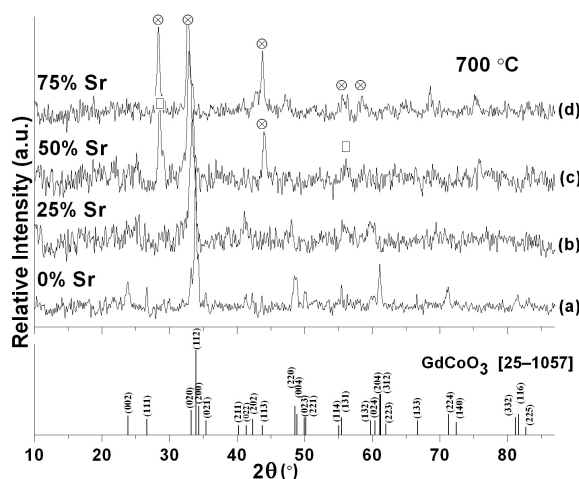


Fig. 19. X-ray diffraction patterns of: (a)  $\text{GdCoO}_3$ , (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ , (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at 700 °C. Schematic presentation of the XRD pattern of  $\text{GdCoO}_3$  from JCPDS is presented at the bottom. The impurity phases are marked:  $\otimes$  –  $\text{SrCoO}_{2.52}$ ,  $\square$  –  $\text{Gd}_2\text{O}_3$ .

Fully crystalline single-phase oxide  $\text{GdCoO}_3$  with the well pronounced perovskite crystal structure have formed at  $800\text{ }^\circ\text{C}$  (see Fig. 20a). In the XRD patterns, having 50 and 75% of Sr, there are peaks attributed to  $\text{SrCoO}_{2.52}$  phase ( $2\theta = 28.531, 32.619, 43.872, 46.713, 55.770$ ). At  $900\text{ }^\circ\text{C}$  temperature despite the main  $\text{GdCoO}_3$  phase there are impurity peaks of  $\text{SrCoO}_3$  (see Fig. 21b and 21c). Growing Sr amount brings more impurity phases to the products. The main phase becomes  $\text{SrCoO}_3$  when there is 75% Sr (see Fig. 21d). It is interesting to note that lattice changes from hexagonal ( $\text{SrCoO}_{2.52}$ ) to cubic ( $\text{SrCoO}_3$ ).

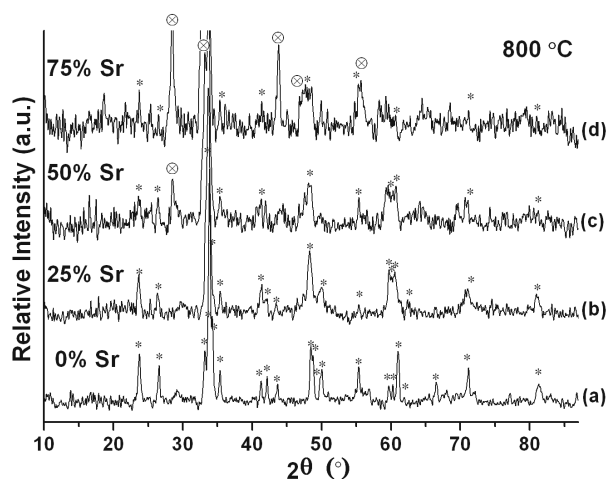


Fig. 20. X-ray diffraction patterns of: (a)  $\text{GdCoO}_3$ , (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ , (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at  $800\text{ }^\circ\text{C}$ . The phases are marked: \* –  $\text{GdCoO}_3$ ,  $\otimes$  –  $\text{SrCoO}_{2.52}$ .

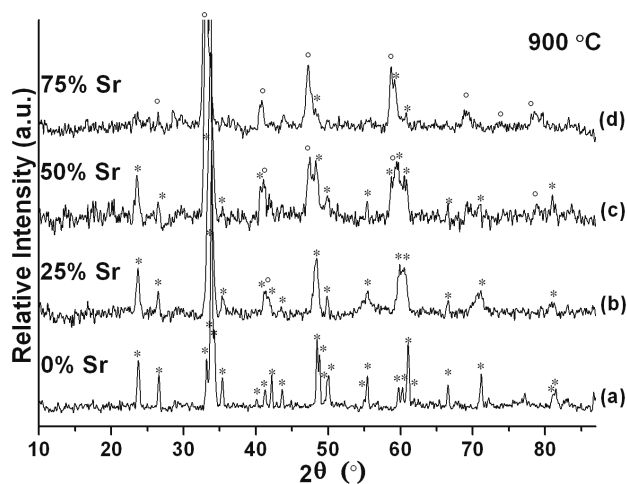


Fig. 21. X-ray diffraction patterns of: (a)  $\text{GdCoO}_3$ , (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ , (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at  $900\text{ }^\circ\text{C}$ . The phases are marked: \* –  $\text{GdCoO}_3$ ,  $\circ$  –  $\text{SrCoO}_3$ .

When ceramic is heated over 900 °C and there is 75% of strontium, the main phase is SrCoO<sub>2.80</sub> (tetragonal lattice), there is no trace of GdCoO<sub>3</sub> (see Fig. 22d, 23d). Probably 1200°C temperature is too-high for good results with bigger amount of Sr (see Fig. 24c, 24d). There can be seen GdCoO<sub>3</sub>, SrCoO<sub>3</sub> (2θ = 22.962, 40.759, 47.280, 53.345, 58.930, 69.138), Co<sub>3</sub>O<sub>4</sub> (2θ = 31.272, 36.853, 65.238) and unknown phases.

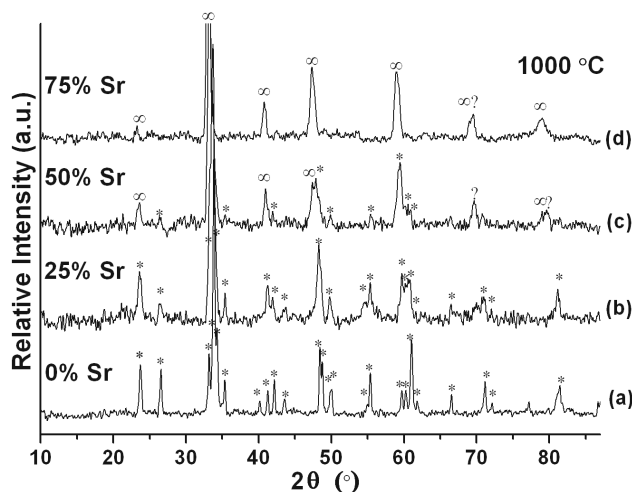


Fig. 22. X-ray diffraction patterns of: (a) GdCoO<sub>3</sub>, (b) Gd<sub>0.75</sub>Sr<sub>0.25</sub>CoO<sub>3-δ</sub>, (c) Gd<sub>0.50</sub>Sr<sub>0.50</sub>CoO<sub>3-δ</sub>, (d) Gd<sub>0.25</sub>Sr<sub>0.75</sub>CoO<sub>3-δ</sub> ceramics prepared at 1000 °C. The phases are marked: \* – GdCoO<sub>3</sub>, ∞ – SrCoO<sub>2.8</sub>, ? – unidentified phases.

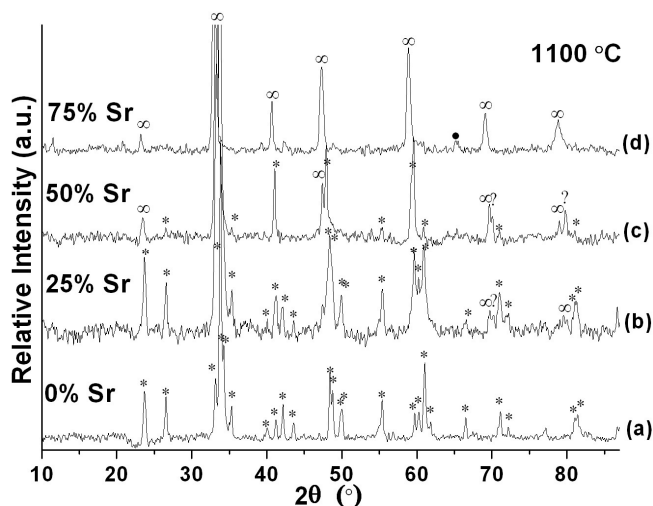


Fig. 23. X-ray diffraction patterns of: (a) GdCoO<sub>3</sub>, (b) Gd<sub>0.75</sub>Sr<sub>0.25</sub>CoO<sub>3-δ</sub>, (c) Gd<sub>0.50</sub>Sr<sub>0.50</sub>CoO<sub>3-δ</sub>, (d) Gd<sub>0.25</sub>Sr<sub>0.75</sub>CoO<sub>3-δ</sub> ceramics prepared at 1100 °C. The phases are marked: \* – GdCoO<sub>3</sub>, ∞ – SrCoO<sub>2.8</sub>, ● – Co<sub>3</sub>O<sub>4</sub>, ? – unidentified phases.

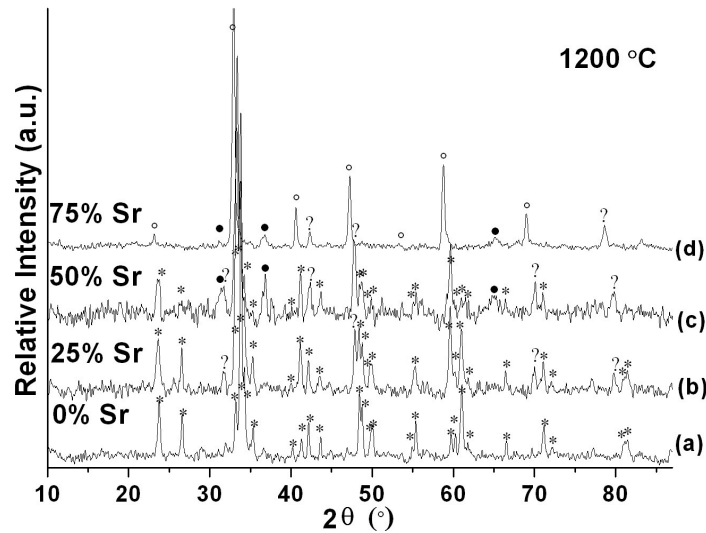


Fig. 24. X-ray diffraction patterns of: (a)  $\text{GdCoO}_3$ , (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ , (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at  $1200\text{ }^\circ\text{C}$ . The phases are marked: \* –  $\text{GdCoO}_3$ , o –  $\text{SrCoO}_3$ , • –  $\text{Co}_3\text{O}_4$ , ? – unidentified phases.

Thus, fully crystalline single-phase oxide  $\text{GdCoO}_3$  has formed in all analyzed temperatures from  $700$  to  $1200\text{ }^\circ\text{C}$ . The XRD patterns of ceramics with  $25\%$  of strontium in the same temperature range show that  $\text{GdCoO}_3$  phase is dominating, but there can be seen  $\text{SrCoO}_{2.8}$  and unknown phases in the samples heated above  $1000\text{ }^\circ\text{C}$  temperature. The amount of impurity phases is growing with rising temperature. Eventually, having  $75\%$  of strontium, the main phase becomes  $\text{SrCoO}_{2.52}$ ,  $\text{SrCoO}_{2.80}$  or  $\text{SrCoO}_3$ . There can be seen  $\text{Co}_3\text{O}_4$  and unidentified impurity phases as well.

Fig. 25 shows the SEM micrographs of  $\text{Gd-Co-O}$  and  $\text{Gd(Sr)-Co-O}$  gels heated at  $1000\text{ }^\circ\text{C}$ . There can be seen irregular form and non-uniform size (to  $1\text{ }\mu\text{m}$ ) particles of  $\text{GdCoO}_3$ .

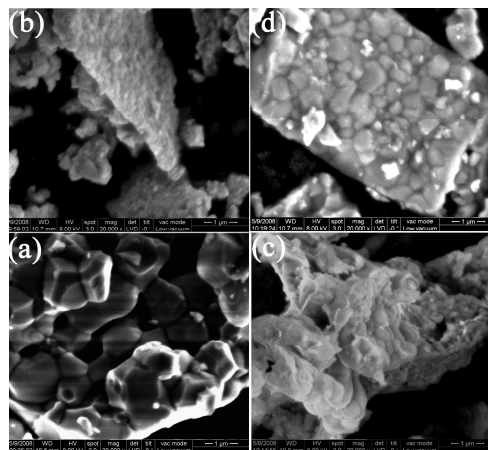


Fig. 25. Scanning electron micrographs of (a)  $\text{GdCoO}_3$  (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ , (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at  $1000\text{ }^\circ\text{C}$ .

When Sr amount has increased (Fig. 25c and d), the particles of different shapes and sizes formed with very well pronounced agglomeration, indicating a good connectivity between the grains. Besides, there can be seen additional particles. It is evident, that morphology of  $\text{GdCoO}_3$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  is different.

### 3.3.2. Synthesis of $\text{GdCoO}_3$ and $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ using other complexing agents

This part reports on the results concerning the sol-gel preparation and characterization of nonsubstituted and Sr-substituted perovskite gadolinium cobaltates  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  and  $0.75$ ). The metal ions, generated by dissolving starting materials (gadolinium oxide, strontium nitrate, cobalt acetate tetrahydrate) in diluted acetic acid were complexed by natural tartaric acid or citric acid to obtain the precursors for the non-substituted and Sr-substituted  $\text{GdCoO}_3$ .  $\text{GdCoO}_3$  and  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50$  or  $0.75$ ) ceramics, prepared using natural tartaric acid or citric acid as complexing agent and heated at  $1000^\circ\text{C}$ , XRD diffractograms are shown in Figs. 26 and 27.

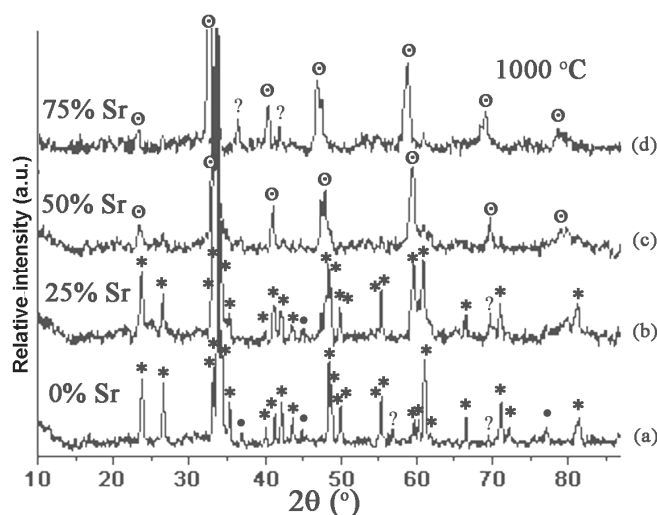


Fig. 26. X-ray diffraction patterns of: (a)  $\text{GdCoO}_3$ , (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$  (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$  (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at  $1000^\circ\text{C}$ , using natural tartaric acid as complexing agent. The phases are marked: \* –  $\text{GdCoO}_3$ ,  $\odot$  –  $\text{SrCoO}_{3-\delta}$ ,  $\bullet$  –  $\text{Co}_3\text{O}_4$ , ? – unidentified phases.

According to X-ray diffraction results, perovskite structure gadolinium cobaltate have formed in the samples without and with 25% strontium, but there are impurity ( $\text{Co}_3\text{O}_4$ , unindented) phases as well. With increasing amount of strontium the main phase becomes  $\text{SrCoO}_{3-\delta}$  in the sample, prepared using natural tartaric acid as complexing agent.  $\text{SrCoO}_{2.8}$  is dominant in the material with 75% of strontium, prepared using citric acid as complexing agent. Increasing strontium amount in the samples forms strontium cobaltate instead of gadolinium cobaltate.

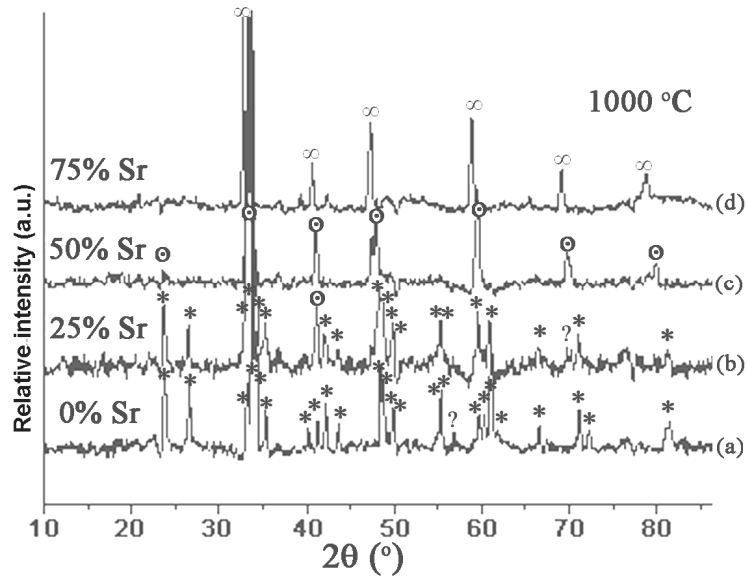


Fig. 27. X-ray diffraction patterns of: (a)  $\text{GdCoO}_3$ , (b)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (c)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$ , (d)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at 1000 °C, using citric acid as complexing agent. The phases are marked: \* –  $\text{GdCoO}_3$ ,  $\odot$  –  $\text{SrCoO}_{3-\delta}$ ,  $\infty$  –  $\text{SrCoO}_{2,8}$ , ? – unidentified phases.

Figs. 28 and 29 show the SEM micrographs of Gd–Co–O and Gd(Sr)–Co–O gels, prepared using natural tartaric acid or citric acid as complexing agent, heated at 1000 °C. There can be seen irregular form volumetric particles in the  $\text{GdCoO}_3$ ,  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$  and  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$  prepared using natural tartaric acid (see Fig. 28). In the samples without strontium or with small amount of it forms 400 nm size and smaller particles. The particles are twice bigger in  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$  and plate-like (to 3  $\mu\text{m}$  size) grains combines monolith structures in  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$ . This can be related with formation of different phases (dependent on the amount of strontium) according to the XRD results.

SEM micrographs are different of samples, prepared using citric acid (Fig. 29). In the case of  $\text{GdCoO}_3$ , the solids compose irregular form non-uniform (500 nm–2  $\mu\text{m}$ ) volumetric particles. There can be seen plate-like 10 nm size and smaller crystallites in the sample with 10% Sr, 100–800 nm – 25% Sr, 400–800 nm – 50% Sr, that are agglomerating and making monolith structures with additional particles on it. It is evident that surface morphology of gadolinium cobaltates and mixed metal cobaltates is different.

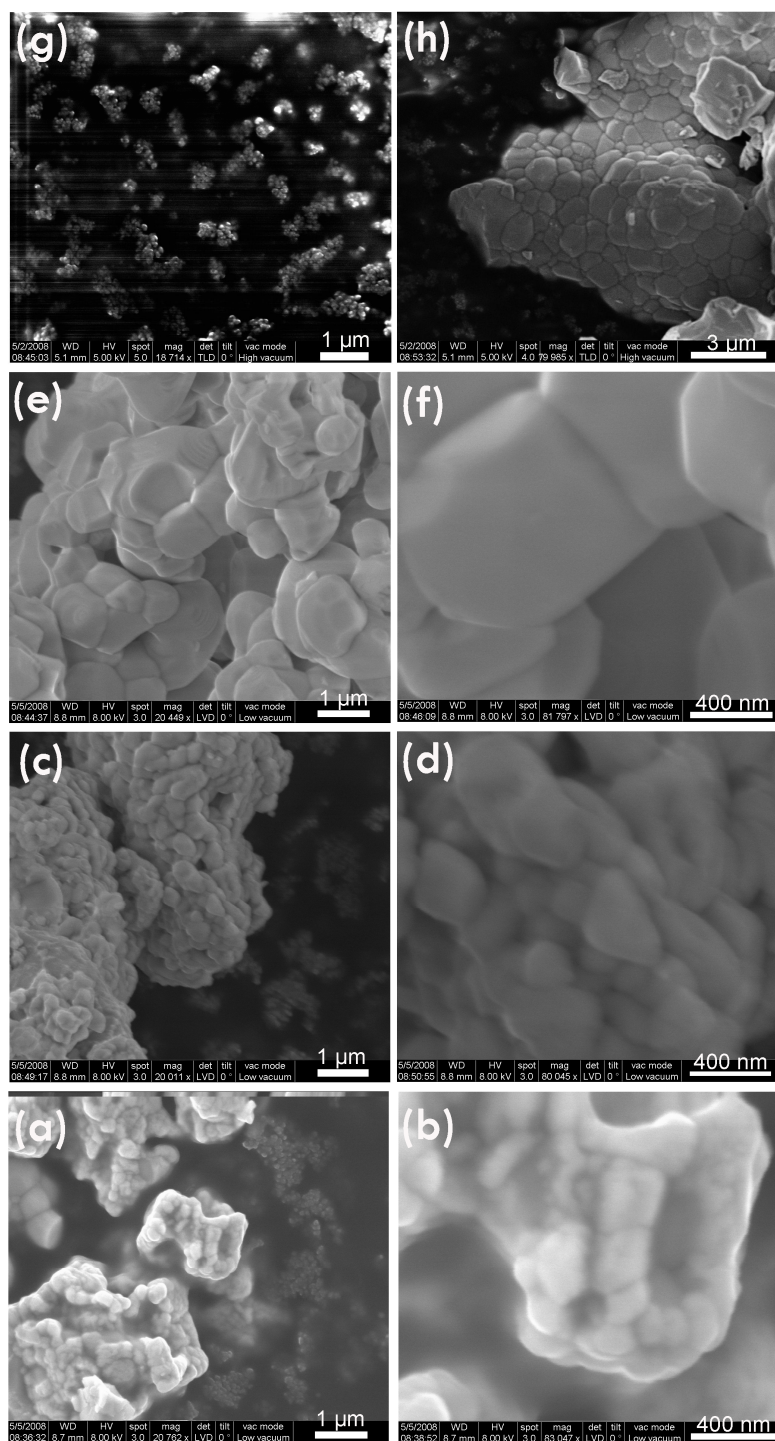


Fig. 28. Scanning electron micrographs of (a and b)  $\text{GdCoO}_3$  (c and d)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$ , (e and f)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$  (g and h)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at 1000 °C using natural tartaric acid as complexing agent. Magnification  $X \sim 20000$  (a, c, e ir g),  $\sim 80000$  (b, d, f ir h).

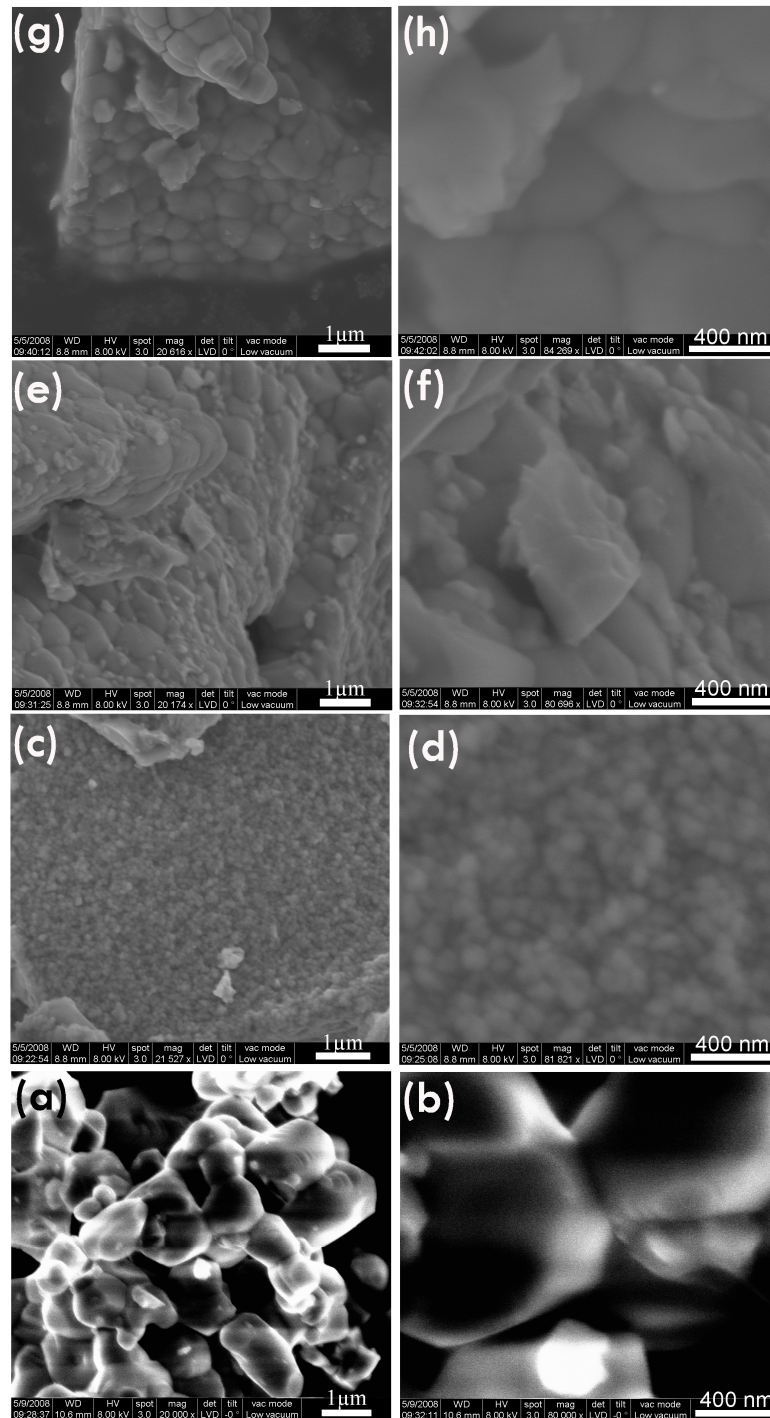


Fig 29. Scanning electron micrographs of (a and b)  $\text{GdCoO}_3$  (c and d)  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$  (e and f)  $\text{Gd}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$  (g and h)  $\text{Gd}_{0.25}\text{Sr}_{0.75}\text{CoO}_{3-\delta}$  ceramics prepared at  $1000^\circ\text{C}$  using citric acid as complexing agent. Magnification  $X \sim 20000$  (a, c, e ir g),  $\sim 80000$  (b, d, f ir h).



## CONCLUSIONS

1. Monophasic perovskite structure gadolinium aluminate  $\text{GdAlO}_3$  has been synthesized by sol-gel synthesis method at  $1000\text{ }^\circ\text{C}$ , using gadolinium oxide as gadolinium raw material and 1.2-ethanediol, natural tartaric acid, citric acid or mixture of citric acid and ethanolamine as complexing agent.
2. According to the XRD results, the  $\text{Gd}_2\text{O}_3$  instead of  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  preferably should be used as starting material for the preparation of  $\text{GdAlO}_3$ .
3. Monophasic perovskite structure strontium substituted gadolinium aluminate  $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{AlO}_{3-\delta}$  was synthesized by the same sol-gel synthesis method at  $1000\text{ }^\circ\text{C}$ , using gadolinium oxide as gadolinium raw material, strontium nitrate as strontium ion source and EDTA as complexing agent.
4. It was proved that better gadolinium ion source is gadolinium oxide than gadolinium nitrate hexahydrate, better complexing agent – EDTA than natural tartaric acid in the synthesis of  $\text{GdAlO}_3$  and strontium substituted  $\text{Gd}_{1-x}\text{Sr}_x\text{AlO}_{3-\delta}$  ( $x = 0.10, 0.25, 0.50, 0.75$ ) samples. According to the XRD results, increasing amount of strontium reduces amount of peaks of perovskite structure gadolinium aluminate. Besides,  $800\text{ }^\circ\text{C}$  temperature is too low for the successful synthesis.
5. An aqueous sol-gel synthesis method for lanthanum and gadolinium cobaltates was suggested for the first time to our knowledge. Monophasic perovskite structure lanthanum cobaltate  $\text{LaCoO}_3$  was synthesized at  $1000\text{ }^\circ\text{C}$ , using lanthanum nitrate as lanthanum raw material, strontium nitrate as strontium ion source and 1.2-ethanediol as complexing agent.
6. Despite increasing amount of strontium and different heating time (3 and 10 h) the main phase was detected of  $\text{LaCoO}_3$  in the  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50, 0.75$ ) samples, heated from  $900\text{ }^\circ\text{C}$ .
7. Monophasic perovskite structure gadolinium cobaltate  $\text{GdCoO}_3$  was synthesized by sol-gel method at  $700\text{--}1200\text{ }^\circ\text{C}$ , using gadolinium oxide as gadolinium raw material, strontium nitrate as strontium ion source and EDTA as complexing agent.
8. Perovskite structure gadolinium cobaltate has formed in the  $\text{GdCoO}_3$  and  $\text{Gd}_{0.75}\text{Sr}_{0.25}\text{CoO}_{3-\delta}$  samples, prepared using gadolinium oxide as gadolinium raw material, strontium nitrate as strontium ion source and natural tartaric acid or citric acid as complexing agent and heated at  $1000\text{ }^\circ\text{C}$ . However the obtained samples were not monophasic.
9. With increasing strontium amount in the  $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $x = 0.25, 0.50, 0.75$ ) samples, synthesized by sol-gel method, the formation of strontium cobaltate instead of gadolinium cobaltate has been observed.

## The List of Original Publications by the Author

### Articles in journals

1. **S. Cizauskaite**, G. Nenartaviciene, A. Beganskiene, A. Kareiva. A comparative study of  $\text{GdAlO}_3$  perovskite prepared with different complexing agents by sol-gel method. *Chemija*, 17 [4] (2006) 40–45.
2. **S. Cizauskaite**, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas and A. Kareiva. Sol-gel preparation and characterization of gadolinium aluminate. *Mater. Chem. Phys.*, 102 (2007) 105–110.
3. **S. Cizauskaite**, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas and A. Kareiva. Sol-gel preparation and characterization of perovskite gadolinium aluminates. *Materials Science (Poland)*, 25 (2007) 755–765.
4. **S. Cizauskaite**, A. Kareiva. Sol-gel preparation and characterization of non-substituted and Sr-substituted lanthanum cobaltates. *Cent. Eur. J. Chem.*, 6 (2008) 456–464.

### Published contributions to academic conference

1. **S. Cizauskaite**, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas, A. Kareiva. Sol-gel preparation and characterization of gadolinium aluminate. Konferencija “Chemija ir cheminè technologija”, Kaunas, Lithuania, 26–27 April (2006).
2. **S. Cizauskaite**, V. Reichlova, G. Nenartaviciene, A. Beganskiene, J. Pinkas, A. Kareiva. Sol-gel preparation and characterization of gadolinium aluminates. 4<sup>th</sup> International Conference on Sol-Gel Materials, Kliczkow Castle, Poland, 18–22 June (2006).
3. **S. Cizauskaite**, G. Spakauskaite. A comparative study of  $\text{GdAlO}_3$  perovskite prepared with different complexing agents by sol-gel method. Conference of Young Chemists of Vilnius University „Inorganic compounds: synthesis, properties and application, Burokaraistele, Varena, Lithuania, 16-17 December 2006, Neorganiniai junginiai: sintezè, savybès ir panaudojimas“, Burokaraistes village, Lithuania, 16–17 December (2006) 10.
4. **S. Cizauskaite**, A. Kareiva. Sol-gel synthesis and characterization of  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ . The 10-th International Conference-School „Advanced materials and technologies“, Palanga, Lithuania, 27–31 August (2008).

## **CURRICULUM VITAE**

### **Sigutė Čižauskaitė**

1999–2003 Bachelor Studies at Vilnius University – Bachelor Degree in Chemistry.

2003–2005 Master Studies at Vilnius University – Master Degree in Chemistry.

2005–2009 Post-graduate studies at the Department of General and Inorganic Chemistry, Faculty of Chemistry of Vilnius University.

2005 (3 months) Internship in Masaryk University, Brno, Czech Republic (Socrates/Erasmus Scholarship).

2008 (3 months) Internship in Aarhus University, Aarhus, Denmark (CIRIUS programme).

## **PEROVSKITO STRUKTŪROS ALIUMINATŲ IR KOBALTATŲ SINTEZĖ ZOLIŲ-GELIŲ METODU**

### **SANTRAUKA**

Šiame darbe gadolinio aluminatas  $GdAlO_3$  buvo susintetinamas zolių-gelių metodu naudojant skirtingas pradines medžiagas bei kompleksus sudarančius reagentus ir iškaitinus  $1000\text{ }^\circ\text{C}$  temperatūroje. Vienfazis perovskito struktūros gadolinio aluminatas  $GdAlO_3$  buvo gautas, gadolinio jonų šaltiniu naudojant  $Gd_2O_3$ , kompleksus sudarančiu reagentu – 1,2-etandiolį, natūralią vyno rūgštį, citrinų rūgštį arba citrinų rūgšties ir etanolamino mišinį. Sintetinant  $GdAlO_3$ , gautų tyrimų rezultatai parodė, kaip yra svarbu zolių-gelių procese pasirinkti tinkamas pradines medžiagas bei kompleksus su metalais sudarančius reagentus: gadolinio jonų šaltiniu naudojant  $Gd_2O_3$  buvo gauti geresni rezultatai nei naudojant  $Gd(NO_3)_3 \cdot 6H_2O$ , vienfazis  $GdAlO_3$  gali būti sėkmingai susintetintas kompleksus sudarančiu reagentu naudojant tiek natūralią vyno rūgštį, tiek 1,2-etandiolį, tiek citrinų rūgštį, tiek citrinų rūgšties ir etanolamino mišinį.

Zolių-gelių metodu naudojant skirtingas pradines medžiagas, skirtingus kompleksus sudarančius reagentus ar jų mišinius bei skirtingas iškaitinimo temperatūras buvo susintetinti gadolinio (stroncio) aluminatai ir jie charakterizuoti TG, DTA, IR spektroskopijos, XRD ir SEM metodais. Nustatyta, kad sintetinant stronciu pakeistus gadolinio aluminatus  $Gd_{1-x}Sr_xAlO_{3-\delta}$  ( $x = 0,10, 0,25, 0,50, 0,75$ ), tinkamesnis gadolinio jonų šaltinis yra gadolinio oksidas nei gadolinio nitratas heksahidratas, kompleksus sudarantis reagentas – EDTA nei natūrali vyno rūgštis. Vienfazis perovskito struktūros stronciu pakeistas gadolinio aluminatas

$Gd_{0,90}Sr_{0,10}AlO_{3-\delta}$  buvo susintetintas zolių-gelių metodu  $1000\text{ }^{\circ}\text{C}$  temperatūroje, gadolinio jonų šaltiniu naudojant  $Gd_2O_3$ , stroncio jonų šaltiniu –  $Sr(NO_3)_2$ , kompleksus sudarančiu reagentu – EDTA. Pastebėta, kad didėjant stroncio kiekiui, XRD difraktogramose aptinkama vis mažiau perovskitiniui gadolinio aluminatui priklausančių smailių. Be to,  $800\text{ }^{\circ}\text{C}$  iškaitinimo temperatūra yra per maža šiems junginiams sintetinti.

Pirmą kartą pasiūlytas vandeninis zolių-gelių metodas lantano ir gadolinio kobaltatams sintetinti. Vienfazis perovskito struktūros lantano kobaltatas  $LaCoO_3$  buvo susintetintas  $1000\text{ }^{\circ}\text{C}$  temperatūroje, lantano jonų šaltiniu naudojant  $La(NO_3)_3$ , stroncio jonų šaltiniu –  $Sr(NO_3)_2$ , kompleksus sudarančiu reagentu – 1,2-etandiolį. Sintetinant  $La_{1-x}Sr_xCoO_{3-\delta}$  ( $x = 0,25, 0,50, 0,75$ ) junginius nustatyta, kad kaitinant gelius  $700\text{--}1000\text{ }^{\circ}\text{C}$  temperatūrų intervale, pagrindinė  $LaCoO_3$  fazė susidaro nuo  $900\text{ }^{\circ}\text{C}$  temperatūros, nepaisant didėjančio stroncio pakeitimo laipsnio ir skirtingos kaitinimo trukmės (3 h ir 10 h). Nustatyta, kad vienfazis perovskito struktūros gadolinio kobaltatas gaunamas zolių-gelių metodu sintetinant gadolinio kobaltatą  $GdCoO_3$   $700\text{--}1200\text{ }^{\circ}\text{C}$  temperatūrų intervale, stronciu pakeistą gadolinio kobaltatą  $Gd_{0,75}Sr_{0,25}CoO_{3-\delta}$   $1000\text{ }^{\circ}\text{C}$  temperatūroje, kai sintezėje gadolinio jonų šaltiniu naudotas  $Gd_2O_3$ , stroncio jonų šaltiniu –  $Sr(NO_3)_2$ , kompleksus sudarančiu reagentu – EDTA. Parodyta, kad  $GdCoO_3$  ir  $Gd_{0,75}Sr_{0,25}CoO_{3-\delta}$  junginiuose susidarė perovskito struktūros gadolinio kobaltatas (gadolinio jonų šaltinis –  $Gd_2O_3$ , stroncio jonų šaltinis –  $Sr(NO_3)_2$ , kompleksus sudarantis reagentas – natūrali vyno rūgštis arba citrinų rūgštis, kaitinimo temperatūra –  $1000\text{ }^{\circ}\text{C}$ ), bet pavyzdžiai nėra vienfaziai. Nustatyta, kad didėjant stroncio kiekiui  $Gd_{1-x}Sr_xCoO_{3-\delta}$  ( $x = 0,25, 0,50, 0,75$ ) junginiuose, susintetintuose zolių-gelių metodu, vietoje gadolinio kobaltato pradeda formuotis stroncio kobaltatai, kurie tampa vyraujančiomis kristalinėmis fazėmis.