



Synthesis and thermal behavior of Co/AlCe layered double hydroxide

Sergei N. Golovin^a, Maksim N. Yaprntsev^a, Irina G. Ryl'tsova^{a,*}, Sergey V. Savilov^{b,c},
Konstantin I. Maslakov^b, Olga E. Lebedeva^a

^a Institute of Pharmacy, Chemistry and Biology, Belgorod State National Research University, 308015, Belgorod, Russian Federation

^b M.V. Lomonosov Moscow State University, Chemistry Department, 119991, Moscow, Leninskie gory, 1, b.3, Russian Federation

^c A.V.Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, 119991, GSP-1, Russian Federation

ARTICLE INFO

Keywords:

Layered compounds
Chemical synthesis
X-ray diffraction
Thermogravimetric analysis
Differential scanning calorimetry

ABSTRACT

Cerium-containing cobalt-aluminum layered double hydroxide was successfully synthesized via coprecipitation followed by hydrothermal treatment. Molar ratios of metal cations were predetermined as following: $\text{Co}^{2+}/(\text{Al}^{3+} + \text{Ce}^{3+}) = 3$ and $\text{Ce}^{3+}/(\text{Al}^{3+} + \text{Ce}^{3+}) = 0.05$. According to X-ray diffraction data, the obtained sample was well crystallized single-phase product with a hydrotalcite-like structure. The presence of cerium was confirmed by elemental analysis. The synthesized material consisted of hexagonal plate-like particles with an average size of 277 nm. The study of thermal behavior showed that the compound decomposed with the formation of oxides mixture, which is typical for layered double hydroxides. Its rehydration ability was expressed very weakly and the “memory effect” was observed only after heat treatment at a temperature not higher than 200 °C.

1. Introduction

Layered double hydroxides (LDHs), also called hydrotalcite-like compounds, are two-dimensional materials consisting of metal hydroxide layers and anions in the interlamellar space (Fig. 1). LDHs can be described by the general formula $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}[\text{A}^{n-}_x/n\text{yH}_2\text{O}]^{x-}$, where M(II) and M(III) are divalent and trivalent metal cations respectively, and A^{n-} is n-valent anion. Interest in this class of compounds remains rather high for a long time due to a wide range of their unique properties [1,2]. Layered double hydroxides have potential applications in catalysis [3,4], drug delivery [5], waste treatment [6], energy storage devices [7], and sensors [8]. The ability of LDHs to vary widely cationic and anionic composition allows obtaining materials with predetermined properties [2].

In recent years researchers focused on LDHs containing transition and rare earth metals, which may exhibit specific catalytic, electrical and magnetic properties. For example, cobalt-containing hydrotalcites are well-known for their catalytic activity [9]. Besides, there are reports on their possible using as supercapacitors for energy conservation processes [10]. Cerium compounds exhibit catalytic activity as well, e.g. they are active in the processes of CO_2 conversion to methane, methanol and in the process of dry methane reforming [11]. CeO_2 is also considered as a potential electrode material for supercapacitors [12,13]. The combination of cerium oxide properties with the advantages of LDH

structure could provide material with unique characteristics.

Incorporation of rare earth elements, e.g. cerium, is still poorly studied. The large ionic radius as well as easy oxidizability of cerium (III) cations makes this objective quite difficult. Zhang et al. reported obtaining Mg/AlCe samples with $\text{Ce}/(\text{Ce} + \text{Al}) = 28.6, 37.5, 44.5$ and 50 mol% [14]. Another Mg/AlCe LDH with $\text{Ce}/(\text{Ce} + \text{Al})$ ratio about 50 mol% was synthesized by Rodrigues et al. [15]. Zhu et al. [16] described the synthesis of Zn/AlCe LDH with $\text{Ce}/(\text{Zn} + \text{Al} + \text{Ce})$ molar ratio of 0.017, 0.05, 0.083 and 0.117. Zn/AlCe LDH with $\text{Ce}/(\text{Ce} + \text{Al})$ molar ratio of 0.05 was obtained by Zhang et al. [17]. Sanati and Rezvani [18] report about synthesis of Ni/AlCe LDH with molar ratio $\text{Ce}/(\text{Ce} + \text{Al}) = 10\%$.

All attempts listed above were not quite successful since the synthesized samples contained extraneous phases, mostly, cerium (IV) oxide CeO_2 . Better results are presented in publication [19]. Mg/AlCe LDHs with $\text{Ce}/(\text{Ce} + \text{Al})$ molar ratios of about 5, 13 and 20 mol% were obtained via coprecipitation method. The sample with 5 mol% of aluminum ions substitution seems to be single-phase. An increase in cerium content up to 13 mol% led to the appearance of an impurity phase in the diffractogram, presumably the phase was cerium (IV) oxide. As the $\text{Ce}/(\text{Ce} + \text{Al})$ molar ratio rose, the crystallinity of the material dropped abruptly. Samples of good quality were obtained by Suarez-Quezada et al. [20] who prepared Zn/AlCe LDHs with $\text{Ce}/(\text{Ce} + \text{Al})$ molar ratio of 3.5, 5 and 10 mol%.

* Corresponding author.

E-mail address: ryltsova@bsu.edu.ru (I.G. Ryl'tsova).

<https://doi.org/10.1016/j.solidstatesciences.2020.106498>

Received 24 July 2020; Received in revised form 23 November 2020; Accepted 24 November 2020

Available online 29 November 2020

1293-2558/© 2020 Elsevier Masson SAS. All rights reserved.

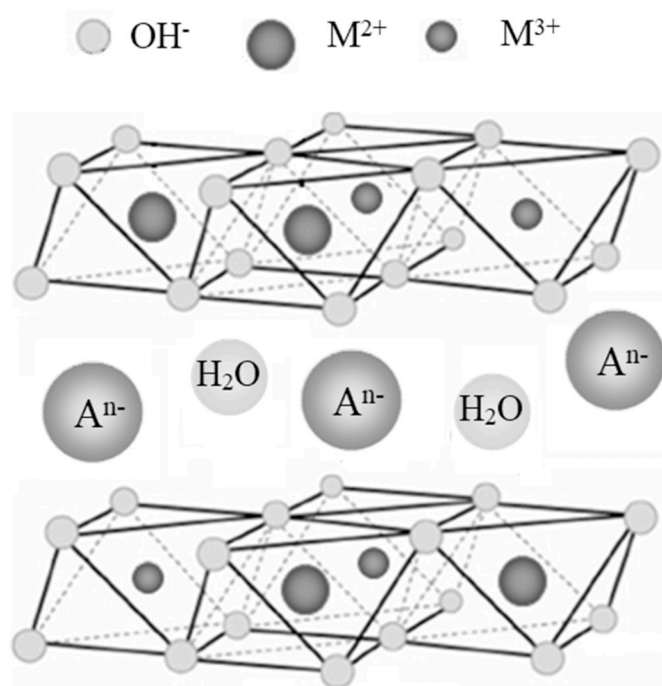


Fig. 1. Schematic view of the LDH structure.

The most successful results were received in syntheses of tetrametallic layered double hydroxides. Wang et al. [21] synthesized single-phase sample with the following composition: Ni_{0.1}Mg_{2.9}Al_{0.95}Ce_{0.05}. Perhaps, the most interesting cerium-containing LDH was obtained by Carja et al. [22]. It was hydrotalcite-like compound with MgCu/AlCe composition, where about 50 mol% of aluminum cations was substituted by cerium.

A number of publications have shown that the introduction of cerium in the composition of the LDH makes it possible to obtain materials with improved properties. So, Zhang et al. reported that the mixed oxides derived by calcination of synthesized LDH precursors demonstrate a higher activity at low temperatures in the reaction of H₂S selective catalytic oxidation than pure CeO₂ [14]. A study of Zhu et al. showed that in comparison with undoped sample, the materials obtained from the LDH of the cerium doped precursor exhibit higher catalytic activity in the photodegradation of rhodamine B [16]. Suarez-Quezada et al. found that the introduction of cerium into the composition of the LDH precursor led to an increase in activity of catalyst in the phenol photodegradation reaction [20].

Recently well crystallized single-phase NiAlCe-LDH was successfully synthesized in our research group by coprecipitation followed by hydrothermal treatment [23]. The molar ratio Ce³⁺/(Ce³⁺ + Al³⁺) was 0.0324. The molar ratio Ni²⁺/(Al³⁺ + Ce³⁺) was found to be 2.597. The present work is a continuation of the previous research. Replacing magnesium cations with cobalt cations was expected to increase the amount of cerium incorporated in the hydrotalcite structure.

2. Experimental

The Co/AlCe hydrotalcite-like compound was obtained by coprecipitation method followed by hydrothermal treatment. Co(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and Ce(NO₃)₃·6H₂O were used as metal precursors. A mixture of NaOH and Na₂CO₃ was chosen as precipitating agent. Reagents were taken in such proportions that the synthesized compound should have the molar ratio M(II)/M(III) = 3 and trivalent cations molar ratio Ce³⁺/(Al³⁺ + Ce³⁺) = 0.05. At the first stage the aqueous solution of nitrates was mixed under vigorous stirring with the precipitant solution. Further the resulting mixture was transferred into autoclave

reactor (Parker autoclave Engineers) for 48 h at 120°C. The synthesized material was centrifuged, washed with distilled water and dried at 110°C for 8 h.

The phase composition of the synthesized sample was verified by powder X-ray diffraction (PXRD). PXRD patterns were recorded on Rigaku Ultima IV diffractometer using CuKα radiation (λ = 1.54056 Å) with 2 deg/min from 2θ = 5°–75° and steps of 0.02. The identification of peaks was made using the PDF database. XRD data were processed by the Rietveld method with integrated X-ray powder diffraction software PDXL (Rigaku Corporation) for determination of lattice parameters [24].

The elemental composition of the obtained material was investigated by the X-ray photoelectron spectroscopy (XPS) using Axis Ultra DLD spectrometer (Al Kα radiation (Ephoton = 1486.7 eV), operating energy was 160 eV for survey spectrum and 40 eV for high-resolution spectrum) and the energy-dispersive X-ray spectrometry (EDX) using the QUANTA 200 3D scanning electron microscope equipped with an energy-dispersive analyzer at the operating voltage of 20 kV. XPS was also used for investigation of electronic state of cerium atoms.

The morphology of the sample was examined with transmission electron microscope JEM-2100 at 200 kV with 0.2 nm resolution.

The behavior of the obtained samples upon heating was studied using an SDT Q 600 combined thermal analyzer able to carry out simultaneously thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses. The investigation was performed in an inert atmosphere in a range of temperatures of 20–1000 °C at a rate of heating of 10 deg/min.

Some portions of hydrotalcite-like material were calcined in air in the microwave muffle furnace Phoenix (CEM) at 200, 300, 400, 500, 600, 700 and 800 °C and their decomposition products were analyzed with PXRD. 0.2 g of samples calcined at 200–600 °C were immersed in 50 ml of distilled water at ambient temperature to estimate their rehydration ability. The samples stayed there for 7 days without stirring. After that, they were dried and investigated by PXRD.

3. Results and discussion

3.1. Phase and chemical composition

The powder X-ray diffraction pattern of the synthesized material looks typical for hydrotalcite-like compounds (Fig. 2). It is isostructural to Co₆Al₂Co₃(OH)₁₆·4H₂O (space group – R-3m (166); JCPDS

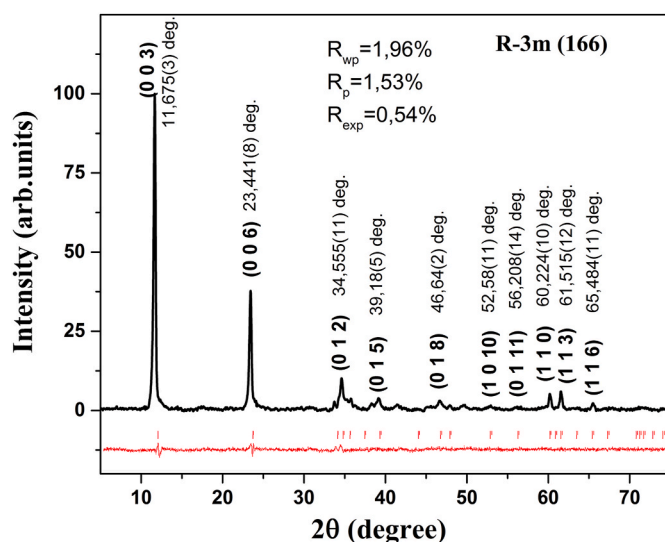


Fig. 2. PXRD pattern of Co/AlCe LDH (calculated Bragg reflections are denoted by vertical ticks).

N^o51–0045). Basal reflections (003), (006), reflections (012), (015) and (018) as well as doublet in a region of 60° with reflections (110) and (113) are characteristic for structures of this type [2]. The sample demonstrates rather high crystallinity in the absence of extraneous reflections.

Determined lattice parameters are: $c = 22.82$ (6) Å and $a = 3.071$ (3) Å. Parameter a corresponds to cation-cation distance in brucite-like layers and depends on ionic radii of cations. Parameter c corresponds to the thickness of the layers and mainly depends on electrostatic interaction between brucite-like sheets and interlamellar anions. The unit cell parameter were calculated as $c = 3 d$ (003) and $a = 2 d$ (110). According to Ref. [25] the parameters a and c for bimetallic Co/Al–CO₃ LDH are equal to 3.07 Å and 22.61 Å respectively. Since the ionic radius of Ce³⁺ (0.102 ± 0.006 nm) was significantly larger than Al³⁺ (0.051 ± 0.003 nm) [26] an increase in the value of parameter a could be expected. However there is no substantial change in this parameter. The result could be accounted for the difference in the M²⁺/M³⁺ ratio. It was equal to 2 in Ref. [25] while it was higher in our case.

EDX spectrum confirms the presence of cobalt, aluminum and cerium in the sample (Fig. 3). The resulting M²⁺/M³⁺ cations molar ratio is lower than originally expected and equals to 2.7 instead of 3. Trivalent cations molar ratio Ce³⁺/(Al³⁺ + Ce³⁺), on the contrary, is slightly larger and amounts to 0.0519.

The presence of cerium in the obtained material was also indicated by survey XPS spectrum (Fig. 4). According to high-resolution spectra cation contents on the surface were found to be 78.3 at.%, 19.9 at.% and 1.8 at.% for Co²⁺, Al³⁺ and Ce³⁺ respectively. Ce3d XPS spectrum (Fig. 5) is typical for trivalent cerium [27]. The line at a binding energy of about 915 eV is not observed, which indicates the absence of contribution to the spectrum from tetravalent cerium within the sensitivity of XPS method [27,28].

3.2. Sample morphology

The transmission electron microscopy data were used to determine the morphology of the synthesized hydrotalcite-like compound (Fig. 6) and its average particle size (Fig. 6). According to it, the sample is represented by hexagonal plate-like particles. LDH crystals are known to grow faster in a or b axis directions and plate-like morphology was observed for multiple LDH of different composition [2,4,8–10,17].

The probability density function P(d) for the distribution in Fig. 7 corresponds to a normal distribution:

$$P(d) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(d-d^*)^2}{2\sigma^2}\right)$$

where d is the current particle size, d^* is the average particle size and σ is

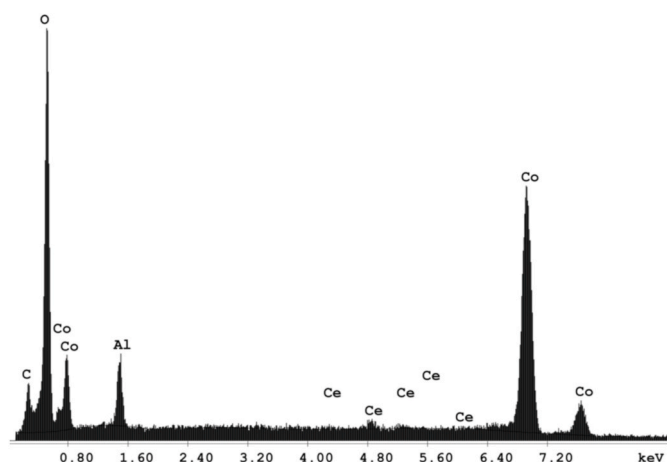


Fig. 3. EDX spectrum of Co/AlCe LDH.

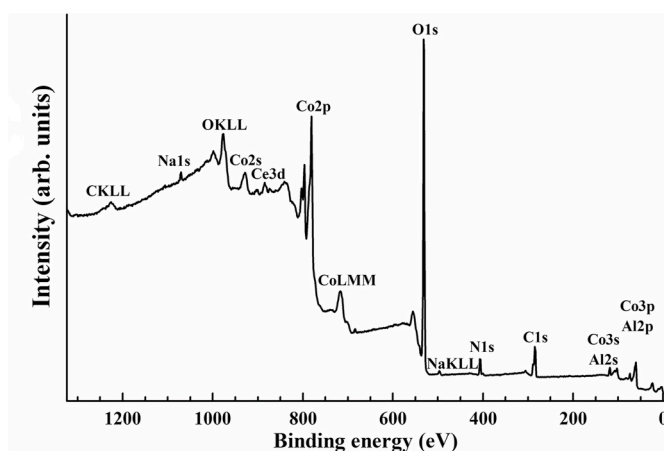


Fig. 4. Survey XPS spectrum of Co/AlCe LDH.

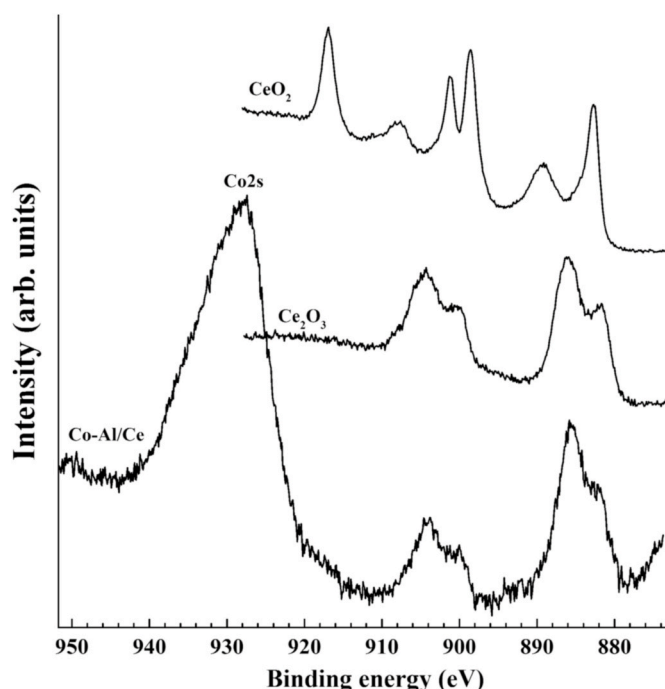


Fig. 5. Ce3d and Co2s XPS spectrum of Co/AlCe LDH. Previously received CeO₂ and Ce₂O₃ spectra are given for comparison.

the standard deviation. Analysis based on the equation allowed to obtain the following values: the average particle size is ≈ 277 nm, the standard deviation is ≈ 71.01 .

3.3. Thermal behavior

The thermal behavior of Co/AlCe LDH sample was examined via thermogravimetric (TGA) analysis and differential scanning calorimetry (DSC) (Fig. 8). Resulting curves are quite typical for compounds with hydrotalcite-like structure [29,30]. Three main processes of weight loss accompanied by endothermic usually take place during LDH thermal decomposition. The first one at 150–220 °C corresponds to the loss of physical absorbed water and crystallization water from interlamellar space. The second and the third processes at 220–450 °C are the dehydroxylation of brucite-like layers and the loss of interlamellar anions. The rise of the DSC curve in a region of 700 °C can be linked to the shrinkage of the sample.

For more detailed study of thermal decomposition certain amounts

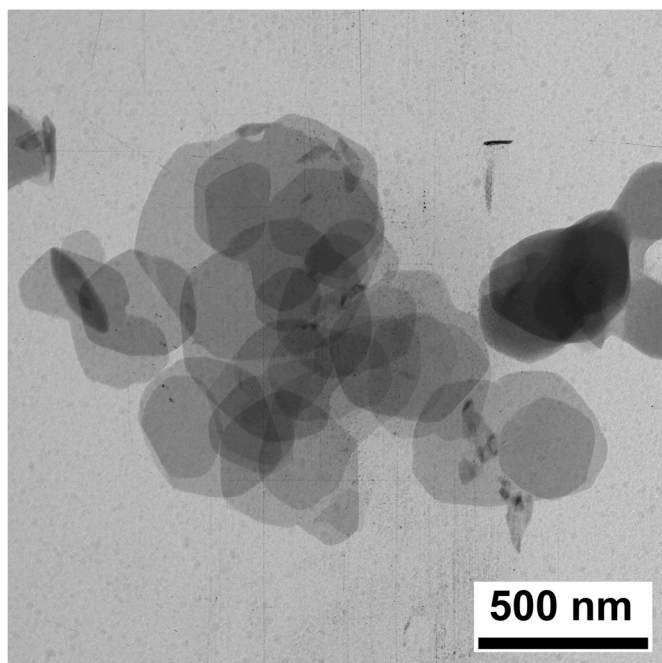


Fig. 6. TEM image of Co/AlCe LDH.

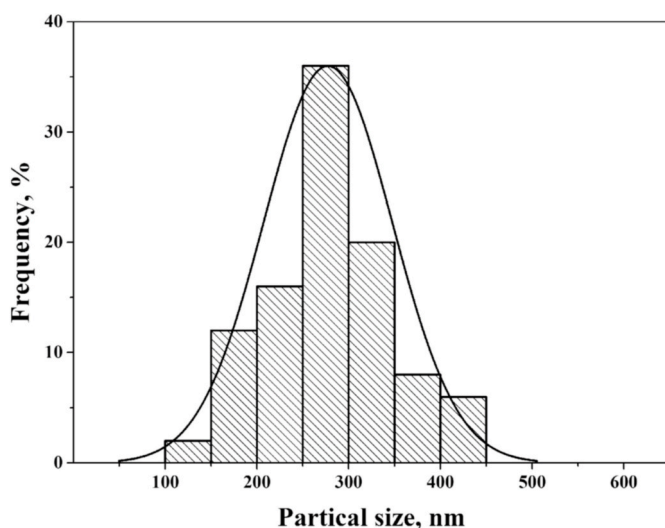


Fig. 7. Particle size distribution for Co/AlCe LDH.

of the synthesized material were calcined in the microwave muffle furnace at different temperatures and the products were analyzed by PXRD method (Fig. 9). Already at 200 °C there is a significant decline of crystallinity and an appearance of extraneous phases. Nevertheless, reflections of hydroxalcalite-like structure are still clearly visible. When the calcination temperature is increased to 300 °C, the whole layered structure decomposes to cerium oxide CeO_2 (space group – Fm-3m (225); JCPDS N^o 01-0800) and spinel-like cobalt-aluminum mixed oxide Co_2AlO_4 (space group – Fd-3m (227); JCPDS N^o 01-1152). A further increase in temperature does not lead to the emergence of new phases, but only improves the crystallinity of formed oxides. Thus, the obtained data have a good correlation with TGA–DSC curves. This behavior during heat treatment is likely to be typical for cobalt-containing LDH. According to the results of reference [31] for CoAl– CO_3 -LDH, which was prepared by hydrolysis of urea, the formation of a metastable phase also occurs after heat treatment at 200 °C, complete destruction of the layered structure is observed already upon heating to

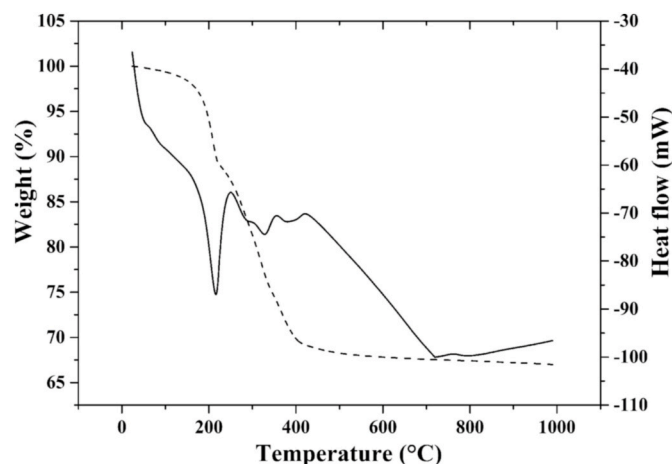


Fig. 8. TGA–DCS curves of Co/AlCe LDH in inert atmosphere (solid curve refers to “Heat flow” and the dashed one – to “Weight”).

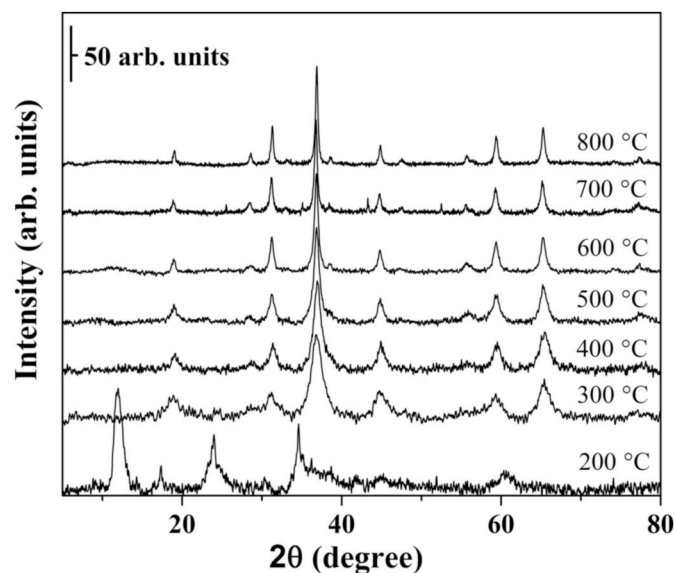


Fig. 9. PXRD patterns of Co/AlCe LDH calcined at different temperatures.

225 °C; an increase in temperature to 275 °C leads to the formation of a spinel phase. In the work [32] for CoAl– CO_3 -LDH, which was prepared by coprecipitation, the layered structure collapses at 200 °C and a solid solution of cobalt spinels (Co_3O_4 , CoAl_2O_4 , or Co_2AlO_4) is formed.

Samples annealed at 200–600 °C were placed in water for several days to estimate their rehydration ability. PXRD patterns show that this procedure had an effect only on the sample that was calcined at 200 °C (Fig. 10). In its case, there is a noticeable improvement in crystallinity, which still remains much lower than it was originally. Also there are weak reflections of impurity phase, presumably, cerium oxide (IV). Samples annealed at 300 °C and above don't demonstrate any perceptible phase transformations after the contact with water in comparison with calcined ones. Apparently, rehydration ability of the obtained compound is limited. It differs from the rehydration behavior of LDH formed by cations in their most stable valent state [33,34]; however it is similar to the results obtained in the publication [32] for cobalt-containing LDH. The authors relate low thermal stability and poor reversibility of Co–Al-LDH calcined at 300 °C to the partial oxidation of Co^{2+} to Co^{3+} during heat treatment. High thermodynamic stability of spinel-like cobalt phases is believed to be the additional reason of the decomposition at low temperature and poor rehydration

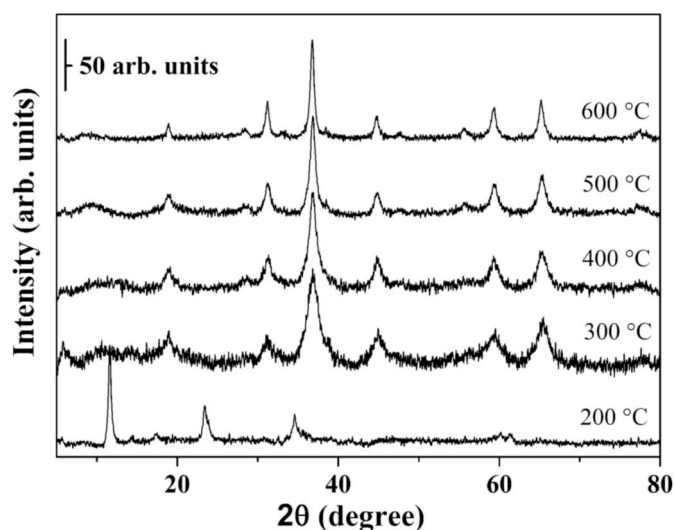


Fig. 10. PXRD patterns of rehydrated Co/AlCe LDH after calcination at different temperatures.

[2,32].

4. Conclusions

In the present work, single phase cerium-containing cobalt-aluminum layered double hydroxide with molar ratio $\text{Ce}^{3+}/(\text{Al}^{3+} + \text{Ce}^{3+})$ equal to 0.0519 was successfully synthesized by coprecipitation method followed by hydrothermal treatment. The presence of cerium was confirmed by the XPS and EDX data. TEM images showed that the obtained powder sample consisted of hexagonal plate-like particles with an average size about 277 nm. The compound started to decompose with the formation of oxides at relatively low temperature. Its ability to recover original layered structure was expressed very weakly and the “memory effect” was observed only during heat treatment at a temperature not higher than 200 °C.

Author statement

Sergei N. Golovin: Investigation, Data curation, Validation, Formal analysis, Writing – original draft. Maksim N. Yaprntsev: Investigation, Data curation, Formal analysis, Writing- Reviewing and Editing, Visualization Irina G. Ryl'tsova: Project administration, Writing – original draft preparation, Reviewing and Editing, Visualization Sergey V. Savilov: Investigation, Data curation, Formal analysis, Writing-Reviewing and Editing Konstantin I. Maslakov: Investigation, Data curation, Formal analysis Olga E. Lebedeva: Conceptualization, Supervision, Methodology, Writing – original draft, Reviewing and Editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The reported study was funded by RFBR according to the research project no. 18-43-310011. The authors are grateful to the staff of the Joint Research Center “Technology and Materials” of Belgorod State National Research University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solidstatesciences.2020.106498>.

References

- [1] G. Mishra, B. Dash, S. Pandey, Layered double hydroxides: a brief review from fundamentals to application as evolving biomaterials, *Appl. Clay Sci.* 153 (2018) 172–186, <https://doi.org/10.1016/j.clay.2017.12.021>.
- [2] F. Cavani, F. Trifiro, A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, *Catal. Today* 11 (1991) 173–301, [https://doi.org/10.1016/0920-5861\(91\)80068-K](https://doi.org/10.1016/0920-5861(91)80068-K).
- [3] G. Fan, F. Li, D.G. Evans, X. Duan, Catalytic applications of layered double hydroxides: recent advances and perspectives, *Chem. Soc. Rev.* 43 (2014) 7040–7066, <https://doi.org/10.1039/c4cs00160e>.
- [4] M. Xu, M. Wei, Layered double hydroxide-based catalysts: recent advances in preparation, structure, and applications, *Adv. Funct. Mater.* 28 (2018) 1802943, <https://doi.org/10.1002/adfm.201802943>.
- [5] Y. Kuthati, R.K. Kankala, C.-H. Lee, Layered double hydroxide nanoparticles for biomedical applications: current status and recent prospects, *Appl. Clay Sci.* 112–113 (2015) 100–116, <https://doi.org/10.1016/j.clay.2015.04.018>.
- [6] B. Zümreoglu-Karan, A.N. Ay, Layered double hydroxides – multifunctional nanomaterials, *Chem. Pap.* 66 (2012) 1–10, <https://doi.org/10.2478/s11696-011-0100-8>.
- [7] M. Sarfraz, I. Shakir, Recent advances in layered double hydroxides as electrode materials for high-performance electrochemical energy storage devices, *J. Energ. Storage.* 13 (2017) 103–122, <https://doi.org/10.1016/j.est.2017.06.011>.
- [8] S.B. Khan, A.A. Asiri, K. Akhtar, M.A. Rub, Development of electrochemical sensor based on layered double hydroxide as a marker of environmental toxin, *J. Ind. Eng. Chem.* 30 (2015) 234–238, <https://doi.org/10.1016/j.jiec.2015.05.027>.
- [9] M. Herrero, P. Benito, F.M. Labajos, V. Rives, Stabilization of Co^{2+} in layered double hydroxides (LDHs) by microwave-assisted ageing, *J. Solid State Chem.* 180 (2007) 873–884, <https://doi.org/10.1016/j.jssc.2006.12.011>.
- [10] X. Long, Z. Wang, S. Xiao, Y. An, S. Yang, Transition metal based layered double hydroxides tailored for energy conversation and storage, *Mater. Today* 19 (2016) 213–226, <https://doi.org/10.1016/j.mattod.2015.10.006>.
- [11] F. Wang, M. Wei, D.G. Evans, X. Duan, CeO_2 -based heterogeneous catalysts toward catalytic conversion of CO_2 , *J. Mater. Chem. A.* 4 (2016) 5773–5783, <https://doi.org/10.1039/C5TA10737G>.
- [12] M. Nallappan, M. Gopalan, Supercapacitor behaviour of cerium oxide nanoparticles in neutral aqueous electrolytes, *Energy Fuel.* 29 (2015) 8246–8253, <https://doi.org/10.1021/acs.energyfuels.5b02144>.
- [13] R. Murugan, G. Ravi, G. Vijayaprasath, S. Rajendran, M. Thaiyan, M. Nallappan, M. Gopalan, Y. Hayakawa, Ni– CeO_2 spherical nanostructures for magnetic and electrochemical supercapacitor applications, *Phys. Chem. Chem. Phys.* 19 (2017) 4396–4404, <https://doi.org/10.1039/C6CP08281E>.
- [14] F. Zhang, X. Zhang, Z. Hao, G. Jiang, H. Yang, S. Qu, Insight into the H_2S selective catalytic oxidation performances on well-mixed Ce-containing rare earth catalyst derived from MgAlCe layered double hydroxide, *J. Hazard Mater.* 342 (2018) 749–757, <https://doi.org/10.1016/j.jhazmat.2017.09.014>.
- [15] E. Rodrigues, P. Pereira, T. Martins, F. Vargas, T. Scheller, J. Correa, J. Del Nero, S. G.C. Moreira, W. Ertel-Ingrisch, C.P. De Campos, A. Giger, Novel rare earth (Ce and La) hydrotalcite like material: synthesis and characterization, *Mater. Lett.* 78 (2012) 195–198, <https://doi.org/10.1016/j.matlet.2012.03.025>.
- [16] J. Zhu, Z. Zhu, H. Zhang, H. Lu, Y. Qiu, L. Zhu, S. Küppers, Enhanced photocatalytic activity of Ce-doped Zn-Al multi-metal oxide composites derived from layered double hydroxides precursors, *J. Colloid Interface Sci.* 482 (2016) 144–157, <https://doi.org/10.1016/j.jcis.2016.07.051>.
- [17] Y. Zhang, J. Liu, Y. Li, M. Yu, X. Yin, S. Li, Enhancement of active anticorrosion via Ce-doped Zn-Al layered double hydroxides embedded in sol-gel coatings on aluminum alloy, *J. Wuhan Univ. Technol.-Materials Sci. Ed.* 32 (2017) 1199–1204, <https://doi.org/10.1007/s11595-017-1731-6>.
- [18] S. Sanati, Z. Rezvani, Co-intercalation of Acid Red-27/sodium dodecyl sulfate in a Ce-containing Ni-Al-layered double hydroxide matrix and characterization of its luminescent properties, *J. Mol. Liq.* 249 (2018) 318–325, <https://doi.org/10.1016/j.molliq.2017.10.145>.
- [19] S. Li, H. Qin, R. Zuo, Z. Bai, Tribological performance of Mg/Al/Ce layered double hydroxides nanoparticles and intercalated products as lubricant additives, *Appl. Surf. Sci.* 353 (2015) 643–650, <https://doi.org/10.1016/j.apsusc.2015.05.091>.
- [20] M. Suárez-Quezada, G. Romero-Ortiz, V. Suárez, G. Morales-Mendoza, L. Lartundo-Rojas, E. Navarro-Cerón, F. Tzompantzi, S. Robles, R. Gómez, A. Mantilla Photodegradation of phenol using reconstructed Ce doped Zn/Al layered double hydroxides as photocatalysts, *Catal. Today Off.* 271 (2016) 213–219, <https://doi.org/10.1016/j.cattod.2016.01.009>.
- [21] L. Wang, B. Li, X. Zhao, C. Chen, J. Cao, Effect of rare earth ions on the properties of composites composed of ethylene vinyl acetate copolymer and layered double hydroxides, *PloS One* 7 (2012), e37781, <https://doi.org/10.1371/journal.pone.0037781>.
- [22] G. Carja, S. Dranca, G. Ciobanu, E. Husanu, I. Balasanian, Fabrication of mesoporous mixed oxides containing copper and cerium by using substituted anionic clays as precursors, *Mater. Sci.-Poland* 27 (2009) 909–917.

- [23] S.N. Golovin, M.N. Yapyrintsev, I.G. Ryltsova, A.A. Veligzhanin, O.E. Lebedeva, Novel cerium-containing layered double hydroxide, *Chem. Pap.* 74 (2020) 367–370, <https://doi.org/10.1007/s11696-019-00877-9>.
- [24] D. Errandonea, R.S. Kumar, O. Gomis, F.J. Manjón, V.V. Ursaki, I.M. Tiginyanu, X-ray diffraction study on pressure-induced phase transformations and the equation of state of ZnGa_2Te_4 , *J. Appl. Phys.* 114 (2013) 233507, <https://doi.org/10.1063/1.4851735>.
- [25] R.E. Johnsen, F. Krumeich, P. Norby, Structural and microstructural changes during anion exchange of CoAl layered double hydroxides: an in situ X-ray powder diffraction study, *J. Appl. Crystallogr.* 43 (2010) 434–447, <https://doi.org/10.1107/S0021889810011805>.
- [26] L.T. Bugaenko, S.M. Ryabykh, A.L. Bugaenko, A nearly complete system of average crystallographic ionic radii and its use for determining ionization potentials, *Moscow Univ. Chem. Bull.* 63 (2008) 303–317, <https://doi.org/10.3103/S0027131408060011>.
- [27] D.R. Mullins, S.H. Overbury, D.R. Huntley, Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces, *Surf. Sci.* 409 (1998) 307–319, [https://doi.org/10.1016/S0039-6028\(98\)00257-X](https://doi.org/10.1016/S0039-6028(98)00257-X).
- [28] N. Thovhogi, A. Diallo, A. Gurib-Fakim, M. Maaza, Nanoparticles green synthesis by Hibiscus Sabdariffa flower extract: main physical properties, *J. Alloys Compd.* 647 (2015) 392–396, <https://doi.org/10.1016/j.jallcom.2015.06.076>.
- [29] V. Prevot, N. Caperaa, C. Taviot-Guého, C. Forano, Glycine-assisted hydrothermal synthesis of NiAl-layered double hydroxide nanostructures, *Cryst. Growth Des* 9 (2009) 3646–3654, <https://doi.org/10.1021/cg900384n>.
- [30] F. Rey, V. Fornés, J.M. Rojo, Thermal decomposition of hydrotalcites. An infrared and nuclear magnetic resonance spectroscopic study, *J. Chem. Soc., Faraday Trans.* 88 (1992) 2233–2238, <https://doi.org/10.1039/FT9928802233>.
- [31] A.V. Radha, G.S. Thomas, P.V. Kamath, C.A. Antonyraj, S. Kannan, Thermal decomposition of Co–Al layered double hydroxide: identification of precursor to oxide with spinel structure, *Bull. Mater. Sci.* 33 (2010) 319–324, <https://doi.org/10.1007/s12034-010-0049-1>.
- [32] J. Pérez-Ramírez, G. Mul, F. Kapteijn, J.A. Moulijn, On the stability of the thermally decomposed Co–Al hydrotalcite against retrotopotactic transformation, *Mater. Res. Bull.* 36 (2001) 1767–1775, [https://doi.org/10.1016/S0025-5408\(01\)00657-2](https://doi.org/10.1016/S0025-5408(01)00657-2).
- [33] Z. Gao, K. Sasaki, X. Qiu, Structural memory effect of Mg–Al and Zn–Al layered double hydroxides in the presence of different natural humic acids: process and mechanism, *Langmuir* 34 (2018) 5386–5395, <https://doi.org/10.1021/acs.langmuir.8b00059>.
- [34] V. Bugris, M. Ádok-Sipiczki, T. Anitics, E. Kuzmann, Z. Homonnay, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálkó, Thermal decomposition and reconstruction of CaFe-layered double hydroxide studied by X-ray diffractometry and 57Fe Mössbauer spectroscopy, *J. Mol. Struct.* 1090 (2015) 19–24, <https://doi.org/10.1016/j.molstruc.2014.10.039>.