



Novel cerium-containing layered double hydroxide

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Abstract

Nickel–aluminum–cerium layered double hydroxide (LDH) in carbonate form was successfully synthesized by co-precipitation followed by hydrothermal treatment. The predetermined molar percentage was the following: $\text{Ni}^{2+}/(\text{Al}^{3+} + \text{Ce}^{3+}) = 3$ and $\text{Ce}^{3+}/(\text{Al}^{3+} + \text{Ce}^{3+}) = 0.05$. The XRD data indicated that the cerium-containing single-phase product with a hydrotalcite structure could be obtained by hydrothermal treatment for 48 h at 120 °C. The transmission electron microscopy analysis showed that the synthesized material consisted of plate-like particles typical for hydrotalcite-like compounds. The average particle size was about 65 nm. The X-ray absorption spectroscopy revealed cerium to be incorporated into the structure of LDH in two different forms, namely 69% of Ce^{3+} and 31% of Ce^{4+} co-existed in the structure.

Keywords Layered double hydroxides · Co-precipitation · Hydrothermal treatment · Cerium

Layered double hydroxides (LDHs), also called hydrotalcite-like compounds, have a two-dimensional structure consisting of metal hydroxide layers and anions in the interlayer space. The general formula of these materials is $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[(\text{A}^{n-})_{x/n} \cdot \text{mH}_2\text{O}]$ (Cavani et al. 1991; Forano et al. 2006). A significant amount of research has been undertaken on the synthesis of LDHs with new compositions over the last decade. The boost is due to the versatility of the properties of the layered double hydroxides. The cationic and anionic composition of layered double hydroxides can vary widely (Cavani et al. 1991; Forano et al. 2006). Thermal treatment leads to the transformation of LDH into a highly dispersed mixture of oxides (Ruano-Casero et al. 2005). Owing to their properties, LDHs can be applied in various fields such as purification of wastewaters, catalysis, and medicine (Zümreoglu-Karan and Ay 2012). In particular, the interest in layered double hydroxides containing rare earth elements in their structure continues to grow. The incorporation of rare earth elements into the structure of layered double hydroxides can generate specific catalytic, electrical and magnetic properties.

However, the incorporation of large rare earth cation, e.g., cerium, into brucite structure is quite a challenge. There are only few publications devoted to the synthesis of cerium-containing bimetallic and polymetallic hydrotalcite-like layered double hydroxides. Suárez-Quezada et al. (2016) described the synthesis of Zn/AlCe LDH with $\text{Ce}/(\text{Ce} + \text{Al})$ ratio 3.5, 5 and 10 mol%. Mg/AlCe LDH with $\text{Ce}/(\text{Ce} + \text{Al})$ ratio about 50 mol% was obtained by Rodrigues et al. (2012); Mg/AlCe samples with $\text{Ce}/(\text{Ce} + \text{Al}) = 28.6, 37.5, 44.5$ and 50 mol% were obtained by Zhang et al. (2018). Polymetallic MgNi/AlCe LDH samples (molar ratio Mg/Ni ~ 2; $\text{Ce}/(\text{Ce} + \text{Al})$ from 4 to 40 mol%) were synthesized by Daza et al. (2011). Recently, the synthesis of Ni/AlCe LDH with molar ratio $\text{Ce}/(\text{Ce} + \text{Al}) = 10\%$ was reported by Sanati and Rezvani (2018). The synthesis was carried out by precipitation with triethylamine in an autoclave without nitrogen.

According to the results presented in the above publications, the synthesized materials are not single-phase products since in the diffractograms of synthesized samples the presence of an extraneous phase can be observed, most likely it is CeCO_3OH or CeO_2 . Single-phase layered double NiMg/AlCe hydroxides were obtained by Wang et al. (2012) for the following composition: $\text{Ni}_{0.1}\text{Mg}_{2.9}\text{Al}_{0.95}\text{Ce}_{0.05}$, with a degree of substitution of aluminum cations by cerium equal to 5 mol%. The attempt made by Carja et al. (2009) seems to be the most successful one; they reported the synthesis of MgCu/CeAl LDH with a degree of substitution of

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magnesium and aluminum cations by copper and cerium, respectively, achieving 50 mol%. Thus, all known pure phase cerium-containing LDH were tetrametallic, while trimetallic cerium LDH always included phase impurities. An additional difficulty in the synthesis of cerium-containing compounds is connected with cerium (III) being easily oxidizable in aqueous solutions.

The main objective of the present study was obtaining single-phase trimetallic layered double hydroxide with a hydroxalite structure containing cerium and aluminum as triply charged cations and only one double-charged nickel cation. Another important task was the determination of the valence of cerium incorporated into the structure of LDH.

The Ni/AlCe hydroxalite-like compound was synthesized by applying the co-precipitation method followed by hydrothermal treatment. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as metal precursors and a mixture of NaOH and Na_2CO_3 served as a precipitating agent. Reagents were taken in proportions to form the compound with molar ratio $\text{M}^{2+}/\text{M}^{3+} = 3$ and trivalent cations molar ratio $\text{Ce}^{3+}/(\text{Al}^{3+} + \text{Ce}^{3+}) = 0.05$. During the synthesis, the aqueous solution of nitrates was mixed by vigorously stirring the precipitant solution. Then the resulting mixture was transferred into the 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. Powder X-ray diffraction patterns were recorded on Rigaku Ultima IV diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$), with $2^\circ/\text{min}$ from $2\theta = 5^\circ$ to 75° and steps of 0.02. The identification of peaks was made using the PDF database. Lattice parameters were calculated by PDXL program (the experimental data were processed by the Rietveld method). The elemental composition of the synthesized sample was investigated by the wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry using the ARL PERFORM'X (Thermo Fisher Scientific) with a rhodium tube at the impulse power of 2.5 kW and an energy-dispersive X-ray spectrometry (EDX) using the QUANTA 3D scanning electron microscope equipped with an energy-dispersive analyzer at the operating voltage of 20 kV. The morphology of the sample was examined with a scanning electron microscope QUANTA 3D and a transmission electron microscope JEM-2100. The oxidation state of cerium cations was estimated by XANES. The measurements of X-ray Absorption Near-Edge Structure (XANES) spectra were performed at the "Structural Materials Science" beamline of the Kurchatov synchrotron radiation source (Chernyshov et al. 2009). The spectra were recorded in fluorescence mode by Amptek X-123 SDD detector at ambient conditions near Ce L_3 edge (5723 eV) with an energy step of 0.6 eV near the edge. Six spectra were recorded and merged to improve measurement statistics.

The powder X-ray diffraction pattern of the obtained sample shown in Fig. 1 looked typical for hydroxalite-like compounds (Cavani et al. 1991; Forano et al. 2006). The synthesized sample was single-phase product; this was confirmed by the absence of extraneous reflexes in the diffraction pattern. The lattice parameters were calculated: $c = 23.15 \text{ \AA}$ and $a = 3.04 \text{ \AA}$. Parameter a corresponds to cation–cation distance in brucite-like sheets 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 interlayer anions. According to data from literature parameters a and c for NiAl– CO_3 LDHs with ratio $\text{M}^{2+}/\text{M}^{3+} = 2.31$ are equal to 3.024 \AA and 22.96 \AA , respectively, and as for ratio $\text{M}^{2+}/\text{M}^{3+} = 3.40$ the parameters are equal to 3.043 \AA and 23.28 \AA , respectively (Koilraj et al. 2012).

An increase in the value of parameter a in our case could be a result of large effective ionic radius of Ce^{3+} ($1.02 \pm 0.006 \text{ \AA}$) in comparison with Al^{3+} ($0.051 \pm 0.003 \text{ \AA}$) (Buganenko et al. 2008) and probably indicated a successful introduction of cerium cations into the structure of brucite-like sheets.

EDX spectrum confirms the presence of nickel, aluminum and cerium in the sample (Fig. 2a). The atom fractions of Ni, Al and Ce calculated from the WDXRF data for the Ni/AlCe LDH differ from those given in the starting synthesis mixture. In the obtained sample, the molar ratio $\text{Ni}^{2+}/(\text{Al}^{3+} + \text{Ce}^{3+})$ was found to be 2.597 and $\text{Ce}^{3+}/(\text{Al}^{3+} + \text{Ce}^{3+})$ was 0.0324.

The morphology of LDH samples was studied by scanning electron microscopy (Fig. 2b) and transmission electron microscopy (Fig. 3a). The Ni/AlCe sample happened to consist of aggregates of plate-like particles typical for

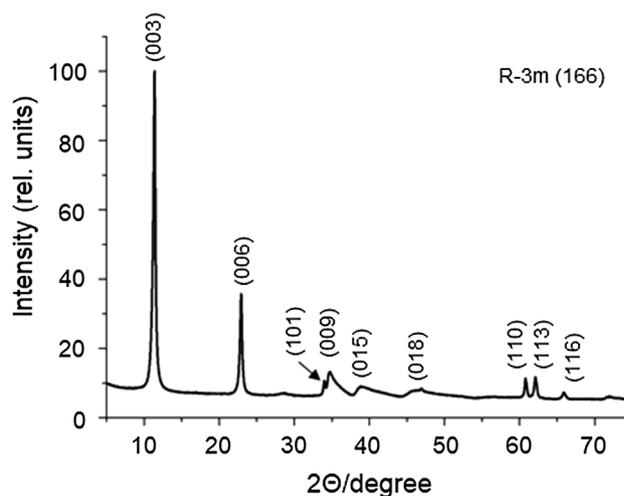


Fig 1 PXRD pattern of Ni/AlCe LDH

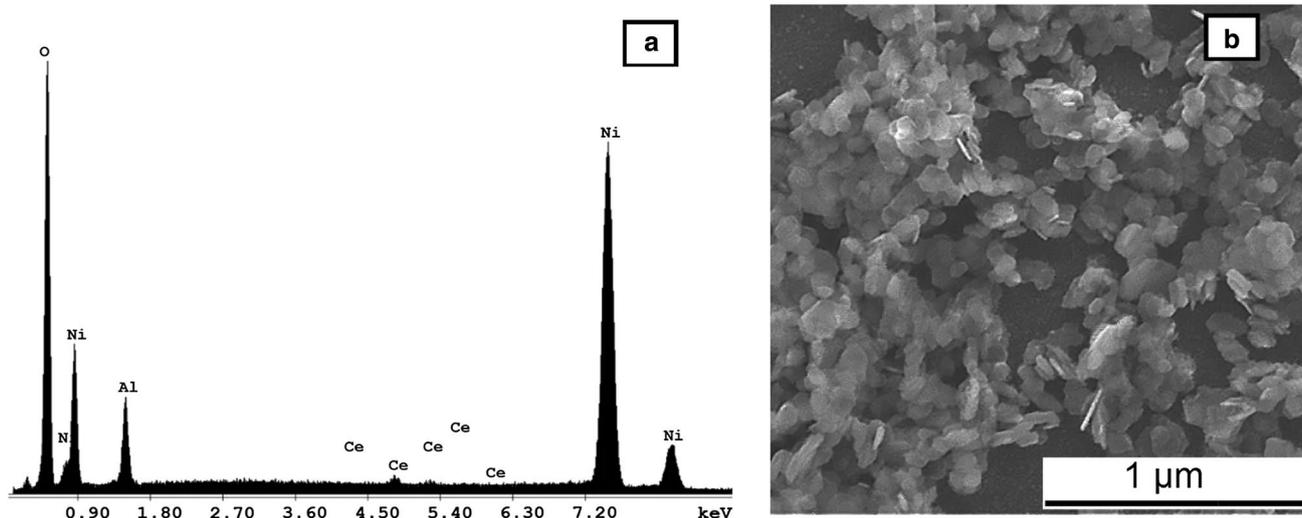
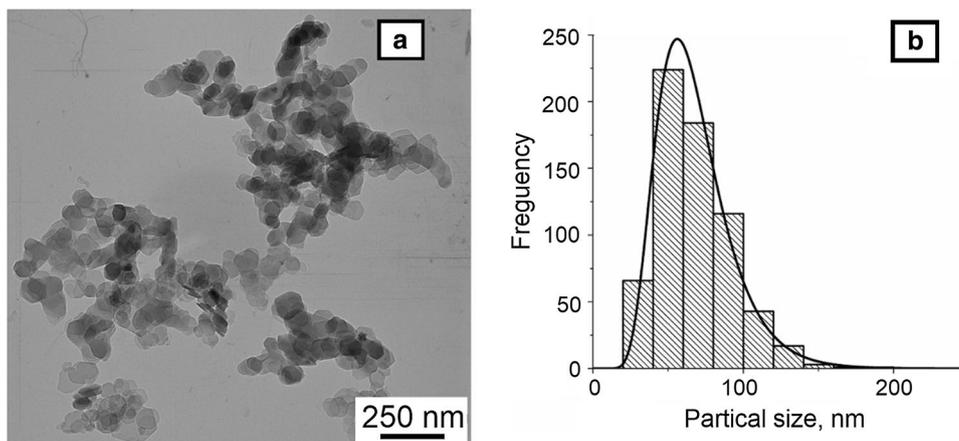


Fig 2 **a** The EDX analysis and **b** SEM images of Ni/AlCe LDH

Fig 3 **a** TEM micrograph of the Ni/AlCe LDH; **b** a histogram of the particle size distribution for the synthesized powder material (the solid black curve corresponds to the log-normal distribution)



the layered structure. TEM data were used to determine the average particle size in the synthesized powder material (Fig. 3b).

It was found that the probability density function $P(d)$ for the distribution in Fig. 3b corresponds to a unimodal log-normal distribution:

$$P(d) = \frac{1}{\sqrt{2\pi}\sigma d} \exp\left(-\frac{(\ln d - \ln \hat{d})^2}{2w^2}\right), \quad (1)$$

where d is the current particle size, \hat{d} is the average particle size, and w is the root-mean-square deviation of the logarithm of the particle size from the mean value (characteristic of the particle size distribution width). The analysis based on expression (1) of the experimental histogram of the particle size distribution in the synthesized powder material allowed

to obtain the following estimates: the average particle size is ~ 65 nm, and the standard deviation is ~ 1.42 .

Figure 4 shows the near-edge region of L_3 Ce (Ce-XANES) for Ni/AlCe LDH and the reference samples. The “white line” is apparently split into two components. This means that a partial Ce^{3+} oxidation occurred giving rise to a mixture of trivalent and tetravalent cerium. The low-energy component is attributed to Ce^{3+} and the higher energy component is attributed to Ce^{4+} which are proved by the spectra of reference compounds $\text{Ce}(\text{NO}_3)_3$ and $\text{Ce}(\text{SO}_4)_2$, respectively, and consistent with the data presented in the paper of Takahashi et al. (2002). The linear combination fitting of the standard spectra to the Ni/AlCe LDH spectrum revealed that content of Ce^{3+} was 69% and Ce^{4+} was 31%.

In this study, single-phase layered double hydroxide with a hydroxalcite structure was successfully prepared by coprecipitation followed by hydrothermal treatment and its structure was verified by XRD. TEM observations showed

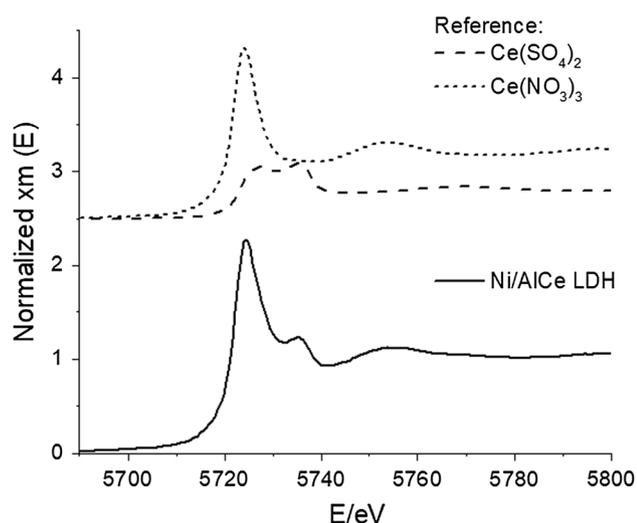


Fig 4 Ce L_3 -edge XANES data for Ni/AlCe LDH

the formation of plate-like nano-sized material containing particles with average size about 65 nm in synthesis conditions. X-ray absorption spectroscopy proved the stabilization of cerium cations in +3 oxidation state in the structure of LDH. During the synthesis and storage, only 31% of cerium cations were oxidized to +4 state.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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