Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Sol–Gel Derived Lanthanide-Substituted Layered Double Hydroxides $Mg_3/Al_{1-x}Ln_x$

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Mg/Al/Ln (Ln = Nd, Sm, Eu) layered double hydroxides (LDHs) were synthesized using sol–gel method for the first time to the best our knowledge. The obtained materials were characterized by X-ray diffraction analysis and fluorescence spectroscopy. The phase composition and luminescent properties of these LDHs were investigated and discussed. The Ln^{3+} substitution effects were investigated in the $Mg_3Al_{1-x}Ln_x$ LDHs by changing the Ln^{3+} concentration in the metal cation layers up to 10 mol%. It was demonstrated that only $Mg_3Al_{1-x}Eu_x$ LDHs showed luminescence properties, however, no any light emission was observed for the $Mg_3Al_{1-x}Nd_x$ and $Mg_3Al_{1-x}Sm_x$ LDH samples.

DOI: 10.12693/APhysPolA.133.884

PACS/topics: 78.66.Fd, 82.70.Gg, 82.33.Ln, 71.20.Eh, 78.55.Hx

1. Introduction

LDHs are compounds with a general chemical formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x^+}(A^{y-})_{x/y} \cdot zH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations and A^y is an intercalated anion which compensates the positive charge created by the partial substitution of M^{2+} by M^{3+} in a brucite-type $M^{2+}(OH)_2$ hydroxide [1]. LDHs are widely used in commercial products as adsorbents, catalyst support precursors, anion exchangers, acid residue scavengers, flame retardants, osmosis membranes, sensors and other [2–4].

Considerable attention has been focused on incorporating of rare earth elements into LDHs host layers to develop new functional materials, which resemble designed optical properties [5–11]. The rare earth doped luminescent materials have drawn increasing attention as potential phosphor materials for use in optical devices [12]. The main aim of this study was to investigate Nd^{3+}, Sm^{3+} and Eu^{3+} substitution effects in the $Mg/Al_{1-x}Ln_x$ systems (the Ln^{3+} concentration in the crystal lattice was changed from 0.05 to 10 mol.%) fabricated for the first time to the best our knowledge by sol–gel synthesis route.

2. Experimental

The Mg/Al and Mg/Al/Ln (Ln = Nd, Sm, Eu) LDH samples were synthesized from solutions of $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ (with molar ratio of 3:1), $Nd(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$ and $Eu(NO_3)_3{\cdot}6H_2O$. The metal nitrates were dissolved in 50 ml of distilled water, then a 0.2 M citric acid solution was added and the mixture was stirred for 1 h at 80 °C. Next, 2 ml of ethylene glycol have been added to the resulted mixture with continuous stirring at 150 °C until the complete evaporation of solvent. The obtained gels were dried at 105 °C for 24 h. The mixed metal oxides (MMO) were obtained by calcination of the gels at 650 °C for 4 h. The Mg/Al and $Mg_3/Al_{1-x}Ln_x$ LDH specimens were obtained by reconstruction of MMO powders in water at 50 °C for 6 h under stirring.

X-ray diffraction (XRD) patterns were recorded using a MiniFlex II diffractometer (Rigaku) in Cu K_α radiation in the 2θ range from 8 to 80° (step of 0.02°) with the exposition time of 0.4 s per step. Excitation and emission spectra were recorded on an Edinburg Instruments FLS 900.

3. Results and discussion

The XRD patterns of synthesized by sol–gel method Mg/Al/Nd 1–10 mol% LDHs are shown in Fig. 1. The LDHs synthesized by sol–gel method were found to be essentially similar to that of standard hydrotalcite. Three basal reflections typical of an LDH structure were observed at 2θ of about 11.5° (003), 23° (006) and 35° (009). Besides, two characteristic LDH peaks were clearly seen at about 60.2° and 61.5° which correspond to the reflections from the (110) and (113) planes. However, the XRD patterns of the Mg/Al/Nd 5 mol.% sample exhibited also reflections of a $Nd(OH)_3$ phase. As seen from Fig. 1, with increase of amount of neodymium the intensity of these diffraction peaks monotonically also increases. XRD patterns of synthesized by sol–gel method

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Mg/Al/Sm 1–10 mol.% LDHs are shown in Fig. 2. Interestingly, the XRD patterns confirm formation of almost single phase Mg/Al/Sm LDH. Only at higher concentrations of samarium (> 7 mol.%) the synthesized samples contained also reflections attributable to the $Sm(OH)_3$ phase. The monophasic Mg/Al/Eu LDHs were also obtained with amount of Eu less than 5 mol.%. With increase of concentration of europium till 7.5 mol.% the negligible amount of side $Eu(OH)_3$ phase has formed. Thus, these results confirmed that highly crystalline lanthanide-substituted LDHs could be synthesized during hydroxylation of sol-gel derived crystalline MMO samples in aqueous media. The lattice parameters of the Mg/Al/Ln LDH samples prepared by sol–gel method were also determined. The lattice parameters grow from about 3.065 to 3.076 Å (a-parameter) and from about 23.699 to 23.899 Å (c-parameter) with increase of amount of lanthanide elements was observed. The obtained crystallographic data suggest that the observed variation in the lattice parameters of the Mg/Al/Ln LDHs are caused by substitution of aluminium by lanthanide elements in the host layers.

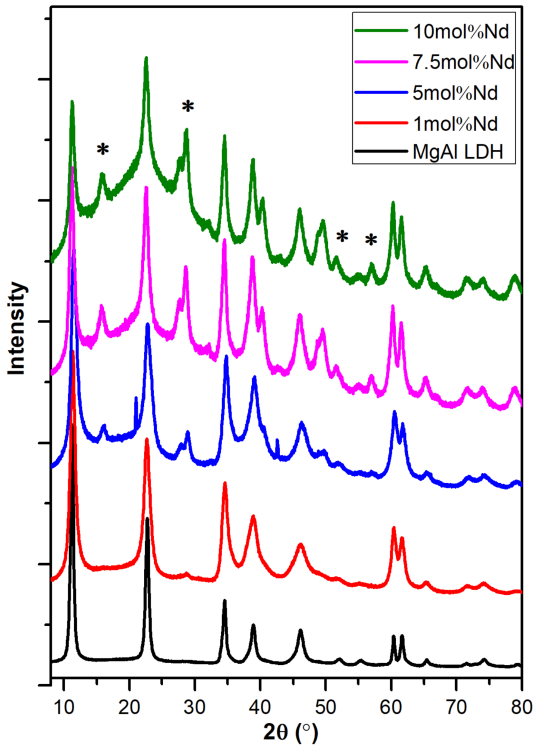

Fig. 1. XRD patterns of synthesized by sol–gel method Mg/Al/Nd 1–10 mol.% LDHs. The $Nd(OH)_3$ phase is marked as $*$.

The luminescent properties of the obtained LDHs were also investigated. The emission spectra obtained at room temperature of all the Mg/Al/Eu LDH samples under excitation at 320 nm are presented in Fig. 3. The emission spectra of Mg/Al/Eu LDHs shows three main emissions in the wavelength range of 500–740 nm. The emis-

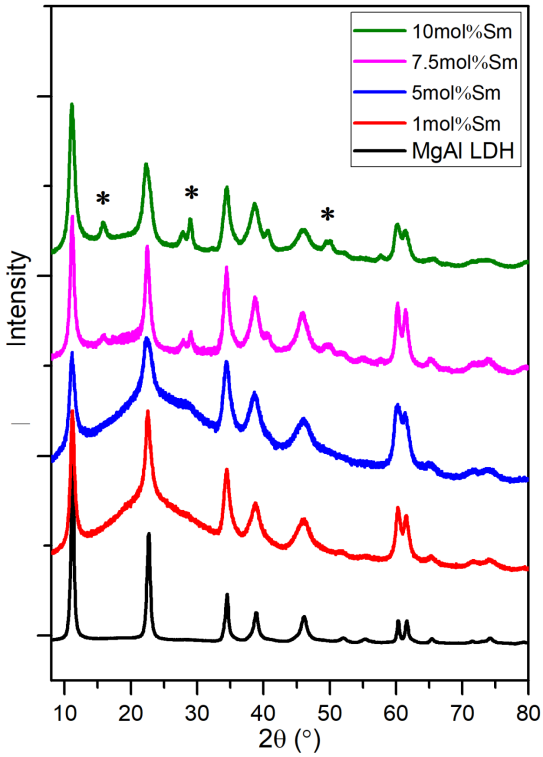

Fig. 2. XRD patterns of synthesized by sol–gel method Mg/Al/Sm 1–10 mol% LDHs. The $Sm(OH)_3$ phase is marked as $*$.

sion peaks are referred to the typical three $^5D_0 \rightarrow {}^7F_1$ (591 nm) $^5D_0 \rightarrow {}^7F_2$ (615 nm) and $^5D_0 \rightarrow {}^7F_4$ (703 nm) transitions of Eu^{3+} ion. The emission due to $^5D_0 \rightarrow {}^7F_2$ transition is the strongest, indicating that Eu^{3+} ions occupy a low-symmetry site. It is clear that the photoluminescence intensity in the Mg/Al/Eu LDH phase increases with increase of the Eu^{3+} concentration, and reaches the maximum when the concentration of Eu^{3+} is 7.5%. With further increasing amount of europium the intensity of emission decreases due to the concentration quenching. Surprisingly, the Mg/Al/Nd and Mg/Al/Sm LDH samples did not show any luminescence. Recently, the organic-inorganic hybrid phosphors have been designed and assembled by the intercalation of organic compounds, as sensitizer, into the layered lanthanide hydroxides or by changing the doping concentration of the activator ions [13–17]. This approach is currently under investigation to stimulate light emission in the Mg/Al/Nd and Mg/Al/Sm LDH samples.

4. Conclusions

The $Mg/Al_{1-x}Ln_x$ (Ln^{3+}–Nd^{3+}, Sm^{3+} and Eu^{3+}) layered double hydroxides (LDHs) with the substitution rate from 0.05 to 10 mol.% were successfully synthesized by sol–gel preparation technique. In this novel aqueous sol–gel processing route, the LDHs were obtained as a result of decomposition (calcination) of the precursor gels at 650 °C followed by rehydration of the intermediate crystalline MMO powders in water. The luminescent prop-

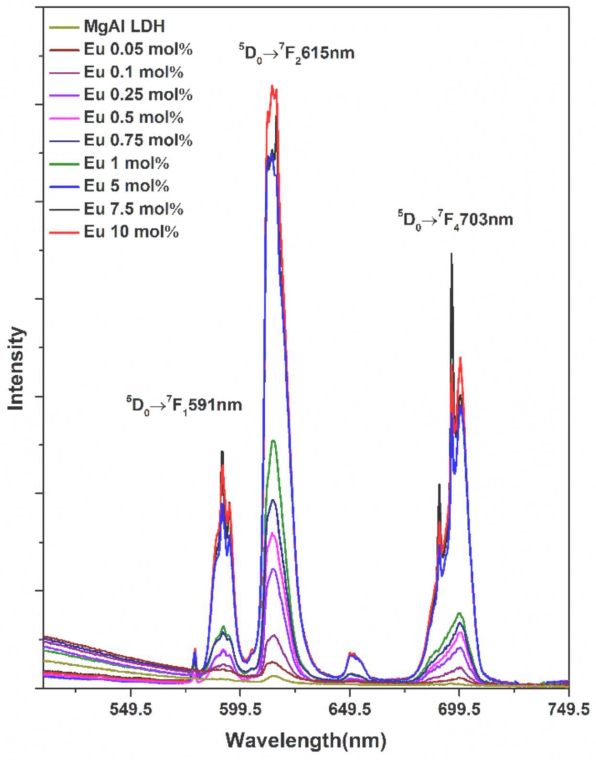

Fig. 3. Photoluminescence emission spectra of Mg/Al/Eu^{3+} LDHs ($\lambda_{ex} = 320$ nm).

erties of the obtained LDHs were also investigated. The emission spectra of Mg/Al/Eu LDHs showed three main emissions in the wavelength range of 500–740 nm corresponding to the typical $^5D_0 \rightarrow ^7F_1$ (591 nm) $^5D_0 \rightarrow ^7F_2$ (615 nm) and $^5D_0 \rightarrow ^7F_4$ (703 nm) transitions of Eu^{3+} ion. However, the Mg/Al/Nd and Mg/Al/Sm LDH samples did not show any luminescence.

Acknowledgments

The work has been done in frame of the project TUMOCS. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 645660.

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