Moroccan Journal of Chemistry
ISSN : 2351-812X

Mor. J. Chem., 2023, Volume 11, Issue 3, Page 756-762
https://revues.imist.ma/index.php/morjchem
https://doi.org/10.48317/IMIST.PRSM/morjchem-v11i3.40224

In-situ Formation of Multimetallic Layered Double Hydroxides and Bayerite/Boehmite/Ceria Composite by Grinding

Muh. Nur Khoiru Wihadi [1]*

[1] *Research Center for Chemistry, National Research and Innovation Agency (BRIN), Republik Indonesia, Kawasan Sains dan Teknologi (KST) B. J. Habibie, Tangerang Selatan 15311, Indonesia*

**Corresponding author, Email address: muh.nur.khoiru.wihadi@brin.go.id*

Received *21 May 2023,*
Revised *02 July 2023,*
Accepted *03 July 2023*

Citation*: Wihadi M.N.K. (2023) In-situ Formation of Multimetallic Layered Double Hydroxides and Bayerite/ Boehmite/Ceria Composite by Grinding, Mor. J. Chem., 14(3), 756-762*

Abstract: Herein, we report three new composites containing multimetallic layered double hydroxides [Ni/Al LDH, Ni.Co/Al LDH, and Ni.Co/Al.Ce LDH] and bayerite/boehmite/ceria. *In-situ* composites formed in a one-pot solid-state reaction and characterization by powder XRD, FT-IR, FE-SEM, and EDS Spectroscopy. The powder XRD and FT-IR spectra indicate the presence of LDH, bayerite, boehmite, or ceria in the solid. The morphological characteristic of the composites demonstrated that the structure was layered material, and the EDS spectra confirmed that the multimetallic components were present in the composite.

Keywords: Grinding; Composite; Layered double hydroxide; *In-situ*

1. Introduction

Layered double hydroxides (LDH) are an attractive family of anionic clays composed mainly of M^{II} (divalent) and M^{III} (trivalent) metal ions that form $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]A^{n-}_{x/n} - ZH_2O$, where A^{n-} is the charge-balancing anion. Their structure comprises brucite-type layers, with the cations (M^{II}/M^{III}) in a net positive charge and the interlayer anion balancing the charge (Fan *et al*. 2014; Kameliya *et al*. 2023). The unique structure of LDH gives it a wide range of potential applications, such as composite material for multifunctional purposes such as catalyst, photocatalysis, water treatment, environmental remediation, removal of greenhouse gases, nutrient storage for plants, biomedical application, biosensor, and supercapacitors (Fan *et al*. 2014; Kameliya *et al*. 2023). Recently, composite material containing LDH has been attracting significant attention; they have been used as adsorbent (Alnasrawi *et al*. 2023; Taher *et al*. 2023), magnetic material (Periyasamy *et al*. 2018), hybrid material with organic and inorganic compounds (Park *et al*. 2023; Capsoni *et al*. 2023; Wihadi *et al*. 2022; Wihadi & Sadakane, 2020; Wihadi *et al*. 2020), catalyst (Men *et al*. 2020; Pavel *et al*. 2020), and ion exchanger (Jobbágy & Regazzoni, 2005; Oestreicher *et al*. 2014; Radha *et al*. 2007). LDH and its composite have been synthesized using various chemical techniques such as hydrothermal (Kloprogge *et al*. 2004), co-precipitation (Miyata, 1975), sol-gel (Lee *et al*. 2016), microwave-aided structure reformation (Benito *et al*. 2007), hydrolysis (Wu *et al*. 2004), and oxide method (Boehm *et al*. 1977). These techniques have many disadvantages including large stages, high energy consumption, and different specialized equipment. As a more straightforward alternative, the mechanochemical method provided simplicity

and versatility (Fahami & Beall, 2016; Pavel *et al*. 2020). This method requires only reactant colliding followed by drying and washing. However, it was rare to synthesize multimetallic layered double hydroxide and its composite using the mechanochemical method. To the best of our knowledge, no information about *in-situ* composite formation containing multimetallic LDH derivatives using mechanochemistry has been reported.

Herein, we report for the first time the *in-situ* composite formation of multimetallic Ni/Al LDH-Bayerite (**1**), Ni.Co/Al LDH-Boehmite (**2**) and Ni.Co/Al.Ce LDH-Ceria (**3**) was prepared via the grinding method in mortar. Furthermore, the structural characterization including crystal phase behavior, functional group, and morphological properties was analyzed by powder XRD, FT-IR spectroscopy, FE-SEM, and EDS spectroscopy. The new composites reported here can be potential candidates for important applications such as water treatment and catalysis.

2. Methodology

2.1 Materials

Homemade deionized water (Millipore) was used. All chemicals were reagent grade and used as supplied.

2.2 In-situ Preparation of Ni/Al LDH-Bayerite (1), Ni.Co/Al LDH-Boehmite (2) and Ni.Co/Al.Ce LDH-Ceria (3)

$Ni(NO_3)_2$-$6H_2O$ (14.54 g (0.05 mol), $Al(NO_3)_3$-$9H_2O$ (37.51 g (0.1 mol) and NaOH 6 g (0.15 mol) for **1**, $Ni(NO_3)_2$-$6H_2O$ (7.27 g (0.025 mol), $Co(NO_3)_2$-$6H_2O$ (7.28 g (0.025 mol), $Al(NO_3)_2$-$9H_2O$ (37.51 g (0.1 mol) and NaOH 6 g (0.15 mol) for **2**, $Ni(NO_3)_2$-$6H_2O$ (7.27 g (0.025 mol), $Co(NO_3)_2$-$6H_2O$ (7.28 g (0.025 mol), $Al(NO_3)_3$-$9H_2O$ (18.76 g (0.05 mol), $Ce(NO_3)_3$-$6H_2O$ (21.71 g (0.05 mol) and NaOH 6 g (0.15 mol) for **3**, respectively were mixed in a mortar and manually ground to a paste for 1 h. The paste was heated at 120 °C for 5 h and washed with deionized water until neutral. The obtained solid was dried at 70 °C for overnight.

2.3 Characterization and Instrumental Analysis

Powder X-ray diffraction (XRD) spectra were recorded on the Panalytical Empyrean diffractometer with Nickel (Ni) filtered Cu Kα radiation (λ= 0.15406 nm) at a current of 30 mA and voltage of 40 kV. The sample was recorded in the 2θ = 0 - 80° with the scanning step length 0.02° per 25 s. The crystal phase was identified using the QUALX 2.0 program (Altomare *et al*. 2015). Infra-red (IR) spectra were obtained on Fourier transform infrared (FT-IR) ATR Bruker Tensor II (USA). The IR spectra of samples were scanned at a wavenumber range of 500 to 4000 cm^{-1} with a resolution of 4.0 cm^{-1} and the number of scans was 45 s. The image and elemental analyses of samples were obtained on the Field Emission Scanning Electron Microscopy Energy Dispersive Spectroscopy (FE-SEM EDS) JEOL JIB 4610F (Japan) equipped with a Schottky electron gun, as well as a new FIB column capable of sizeable current processing (maximum ion current of 90 nA) installed into one chamber.

3. Results and Discussion

Figure 1a shows the powder XRD pattern of **1**, **2** and **3** composites prepared mechanochemically in mortar. The XRD pattern of **1, 2,** and **3** shows sharp diffraction peak at [2θ = 11.33°, 22.79°, 35.07° and 61.12°], [2θ = 11.45°, 22.86°, 34.89° and 60.55°], and [2θ = 11.29°, 22.77°, 35.40° and 61.08°], respectively assigned to basal planes {003}, {006}, {009} and {110} indicating LDH presence in the solid. The broad diffraction peak of **1** reveal at 2θ = 18.72°, 20.27°, 27.78°, 40.50°, and 53.12° assigned

to bayerite species. In case of **2** and **3**, the broad diffraction peak observed at [2θ = 14.37°, 28.19°, 38.55°, and 48.87°], and [2θ = 33.93°, 40.53°, 47.51°, and 56.48°] confirmed to boehmite and CeO_2 species, respectively. The presence of Ni/Al LDH, bayerite, boehmite and CeO_2 (ceria) in the compounds was confirmed by the standard for LDH (PDF No. 00-210-2792), bayerite (PDF No. 00-900-8135), boehmite (PDF No. 00-901-2247), and CeO_2 (PDF No. 00-434-3161) assignment, respectively (**Figure 1b**, **1c**, and **1d**).

The XRD pattern of **1**, **2** and **3** confirmed the successful preparation of Ni/Al LDH, Ni.Co/Al LDH and Ni.Co/Al.Ce LDH, which was shown by the presence of a diffraction pattern assigned to basal planes {003}, {006}, {009} and {110} (Fahami & Beall, 2016; Taher *et al*. 2023). The formation of bayerite (β-$Al(OH)_3$) and boehmite (γ-AlOOH) in **1** and **2** was influenced by the transformation of Al^{3+} during the reaction. Tsuchida and Ichikawa reported the mechanochemical transformation phenomena of gibbsite, bayerite, and boehmite by grinding (Tsuchida & Ichikawa, 1989). In our case, the transformation of Al^{3+} to bayerite and boehmite occurred during the grinding of the precursor in mortar. Therefore, LDH products are found with a mixture of Al^{3+} derivatives. In the similar case of **3**, the presence of the side product (CeO_2) was also observed with the main product of Ni.Co/Al.Ce LDH.

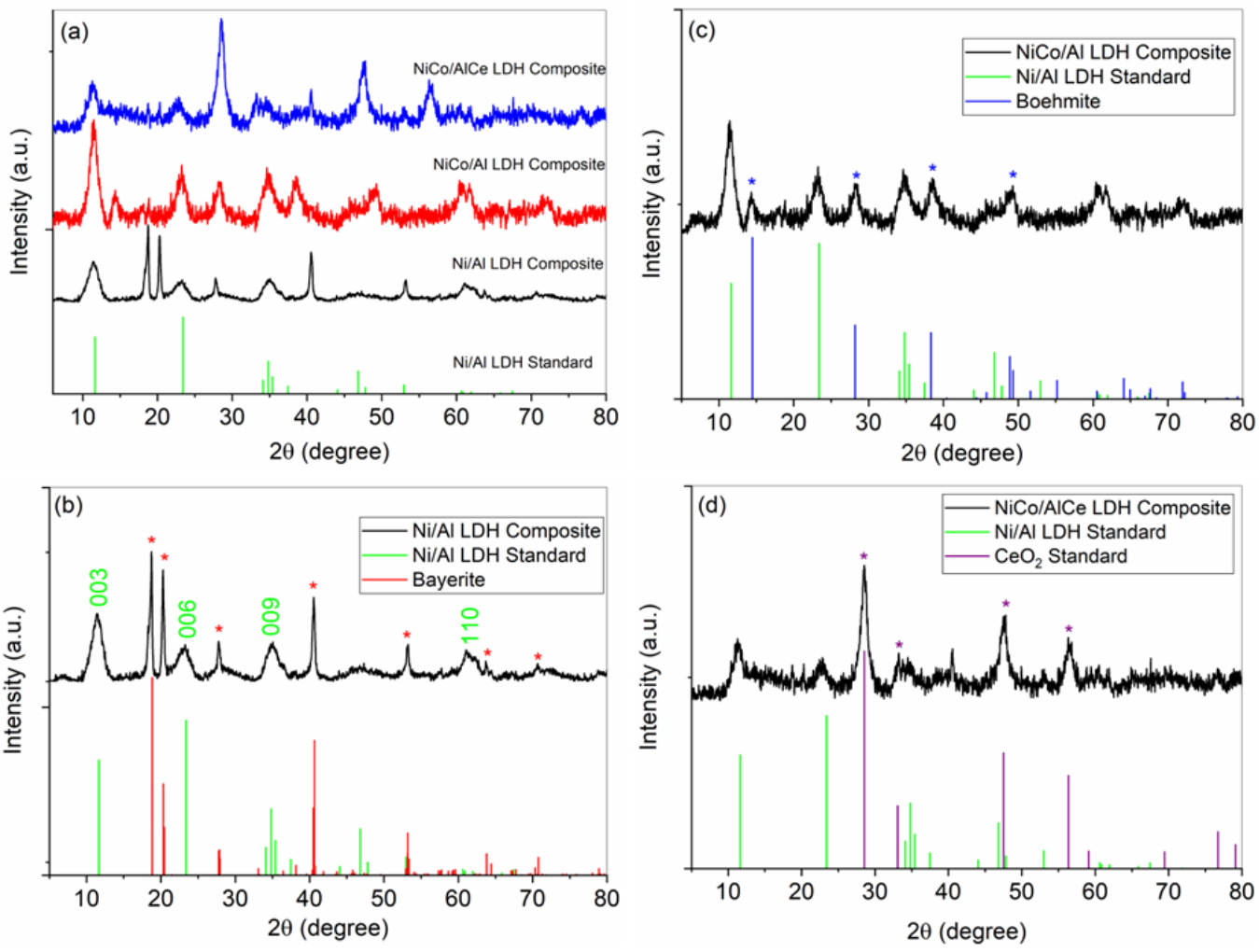

Figure 1. Powder XRD pattern of a solid containing multimetallic layered double hydroxide (LDH) composites and assignment with the profile of LDH Standard (PDF No. 00-210-2792) (a). Composite assignment with bayerite (PDF No. 00-900-8135) (b), boehmite (PDF No. 00-901-2247) (c), and CeO_2 standards (PDF No. 00-434-3161) (d). The red, blue, and violet stars correspond to the bayerite, boehmite, and CeO_2.

Figure 2 shows the IR spectra of the composites which displayed similar countenance for the LDH samples. The bands at 3517.78 cm^{-1} (**1**), 3420.10 cm^{-1} (**2**) and 3545.22 cm^{-1} (**3**) are identified to -OH vibration stretching modes. The bending vibration of the interlayer water was displayed at 1641.52 cm^{-1} (**1**), 1643.28 cm^{-1} (**2**) and 1642.10 cm^{-1} (**3**). The bands at 657.92 cm^{-1} (**1**), 654.11 cm^{-1} (**2**) and 650.62 cm^{-1} (**3**) were assigned to Ni-O and Al-O stretching modes. In the case of **2** and **3**, Co-O and Ce-O stretching modes were also observed. Composites **1**, **2**, and **3** have similar morphologies (**Figure 3**). The composite showed hexagonal platelet-type morphology. Bayerite, boehmite, and CeO_2 species in the product facilitate non-uniform platelet. The layered structure of the composite can be displayed in FE-SEM images (**Figure 3**) (Fahami & Beall, 2016; Taher *et al*. 2023).

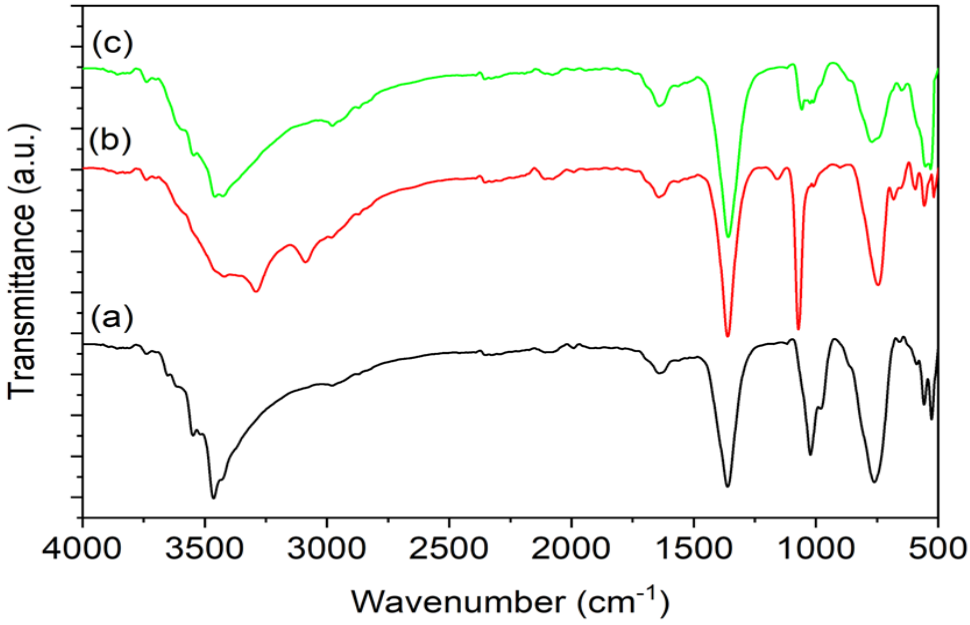

Figure 2. IR Spectra of the solid containing the Ni/Al LDH-Bayerite composite (a), Ni.Co/Al LDH-Boehmite composite (b), and Ni.Co/Al.Ce LDH-Ceria composite (c).

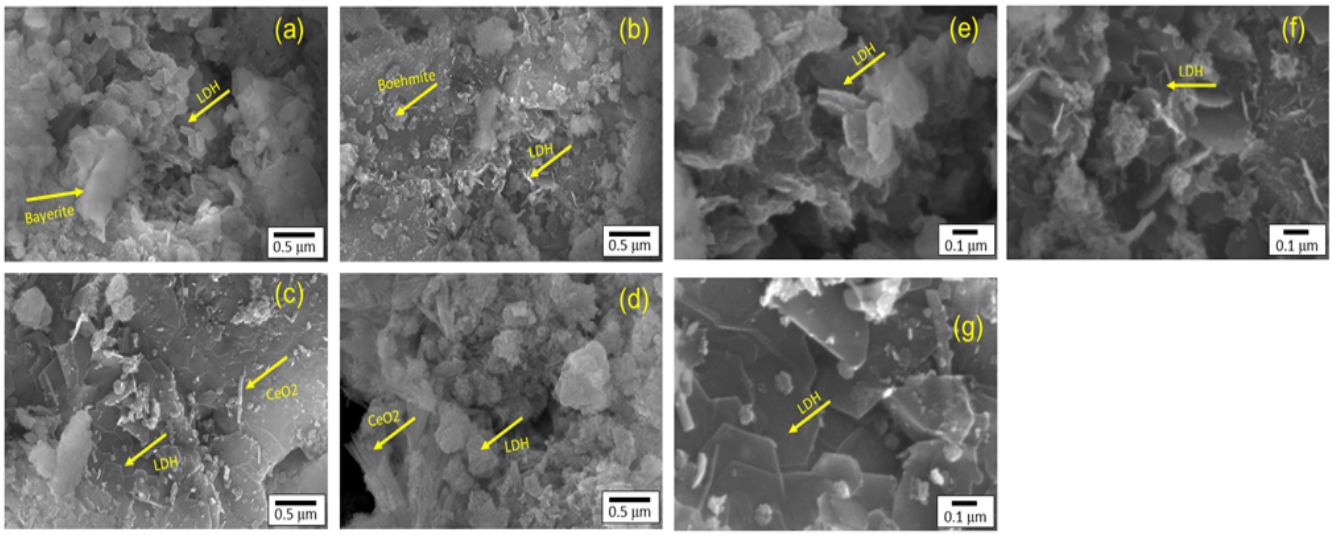

Figure 3. Field emission scanning electron microscope (FE-SEM) images of composite **1** (a), **2** (b), **3** (c) and (d). The other magnification of 100,000x for composite **1** (e), **2** (f) and **3** (g). FE-SEM data showed clear images of LDH, bayerite, boehmite and CeO_2 in the solid.

The EDS elemental analysis of the composites (**Figure 4**) revealed that the main elements of the composite were nickel, aluminum, nitrogen and oxygen (composite **1**). The other elements, such as cobalt and cerium, also detect for composite **2** and **3**, respectively. No other contaminants were observed. The layered diameter distribution size was 76.02 nm, 92.01 nm and 180.38 nm for composites **1**,**2,** and **3**, indicating the introduction of multimetallic elements (Co and Ce) in the layered structure influenced the size of the material to be larger. The EDS map also demonstrated the distribution of the heavy elements such as cerium in composite **3** detected not only as CeO_2 but present in the layered structure of the LDH, indicating the cerium substituted Al^{3+} position in the layered framework. The ability of cerium substituted ion in the framework also found in other material such as TiO_2 (Elafia *et al*. 2023; Lerari & Benaboura, 2015).

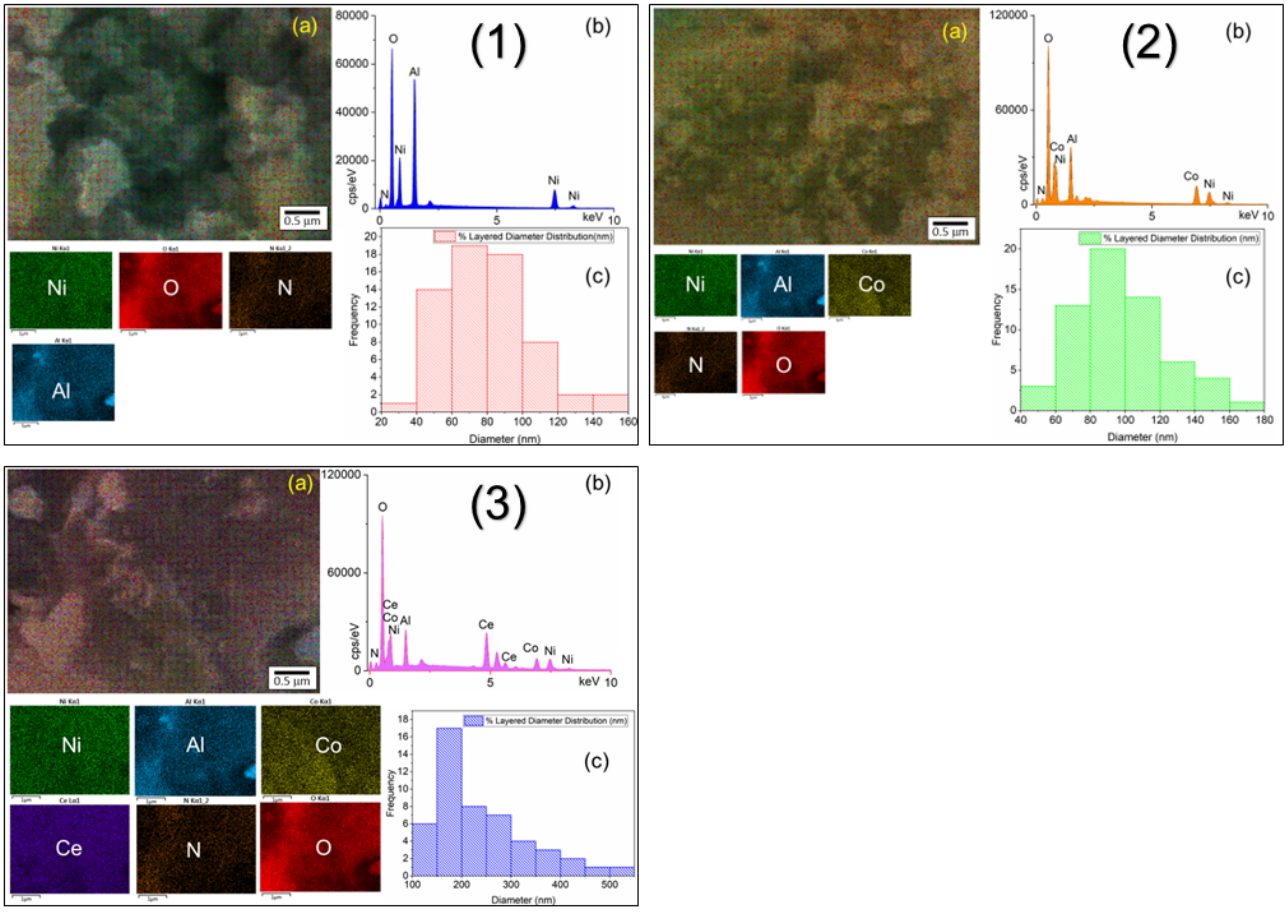

Figure 4. EDS elemental distribution map (a), EDS spectrum (b) and histogram of layered diameter distribution (c) of composite **1**, **2**, and **3**, respectively.

Conclusion

In this study, three new composites containing multimetallic layered double hydroxides [Ni/Al LDH, Ni.Co/Al LDH, and Ni.Co/Al.Ce LDH] and bayerite/boehmite/ceria successfully prepared by grinding method in mortar. The presence of LDH and its composite was confirmed by the powder XRD and FT-IR spectroscopy. The structure of the new composites was layered materials confirmed by FE-SEM. The EDS spectra indicated the presence of multimetallic components in the composite.

Acknowledgement: This research was supported by Rumah Program (RP) Organisasi Riset Nanoteknologi dan Material, National Research and Innovation Agency (BRIN) No. 3/III.10/HK/2023 Code 52. We thank

Mr. Nanang Hamzah from Tadulako University for the initial preparation of the nanocomposite during the internship program. We gratefully acknowledge the support from Advanced Characterization Laboratories Serpong, National Research and Innovation Agency (BRIN), through E-Layanan Sains (ELSA).

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References

Alnasrawi F. A., Mohammed A. A., & Al-Musawi T. J. (2023). Synthesis, characterization and adsorptive performance of CuMgAl-layered double hydroxides/montmorillonite nanocomposite for the removal of Zn(II) ions. *Environ. Nanotechnol. Monit. Manag.*, *19*, 100771-100783 https://doi.org/10.1016/j.enmm.2022.100771

Altomare, A., Corriero, N., Cuocci, C., Falcicchio, A., Moliterni, A., & Rizzi, R. (2015). QUALX2.0: A qualitative phase analysis software using the freely available database POW-COD. *J. Appl. Crystallogr.*, *48*, 598–603. https://doi.org/10.1107/S1600576715002319

Benito, P., Guinea, I., Herrero, M., Labajos, F. M., & Rives, V. (2007). Incidence of microwave hydrothermal treatments on the crystallinity properties of hydrotalcite-like compounds. *Z. Anorg. Allg. Chem.*, *633*(11–12), 1815–1819. https://doi.org/10.1002/zaac.200700178

Boehm, H. P., Steinle, J., Vieweger, C. (1977). $[Zn_2Cr(OH)_6]X.2H_2O$, New Layer Compounds Capable of Anion Exchange and Intracrystalline Swelling. *Angew. Chem. Int. Ed. 16*, 265-266.

Elafia, Z., Messous, M.Y., Hammouti, B., & Cherkaoui, M. (2023). Synthesis and characterization of Mn/Ce-Doped TiO_2: Investigation of structural and optical properties. *Mor. J. Chem.*, *2023*(2), 350–360. https://doi.org/10.48317/IMIST.PRSM/morjchem-v11i2.35078

Fahami, A., & Beall, G. W. (2016). Mechanosynthesis and characterization of Hydrotalcite like Mg-Al-SO4-LDH. *Mater. Lett.*, *165*, 192–195. https://doi.org/10.1016/j.matlet.2015.11.132

Fan, G., Li, F., Evans, D. G., & Duan, X. (2014). Catalytic applications of layered double hydroxides: Recent advances and perspectives. *Chem. Soc. Rev.*, *43*, 7040–7066. https://doi.org/10.1039/c4cs00160e

Jeong, Y. K., Lee, S.-B., Kweon, S., Jeong, J., Park, M. B., Oh, J.-M., & Park, J. K. (2023). Synergistic Inorganic/Inorganic Hybrid Approach for Fabricating a BTX Gas Adsorbent with High Performance and Thermal Stability. *ACS Sustain. Chem. Eng.*, https://doi.org/10.1021/acssuschemeng.2c06591

Jobbágy, M., & Regazzoni, A. E. (2005). Anion-exchange equilibrium and phase segregation in hydrotalcite systems: Intercalation of hexacyanoferrate(III) ions. *J. Phys. Chem. B.*, *109* (1), 389–393. https://doi.org/10.1021/jp046063b

Kameliya, J., Verma, A., Dutta, P., Arora, C., Vyas, S., & Varma, R. S. (2023). Layered Double Hydroxide Materials: A Review on Their Preparation, Characterization, and Applications. *Inorganics*, *11*(3), 121. https://doi.org/10.3390/inorganics11030121

Kloprogge, J. T., Hickey, L., & Frost, R. L. (2004). The effects of synthesis pH and hydrothermal treatment on the formation of zinc aluminum hydrotalcites. *J. Solid State Chem.*, *177*(11), 4047–4057. https://doi.org/10.1016/j.jssc.2004.07.010

Lee, G., Kang, J. Y., Yan, N., Suh, Y. W., & Jung, J. C. (2016). Simple preparation method for Mg–Al hydrotalcites as base catalysts. *J. Mol. Catal. A Chem.*, *423*, 347–355. https://doi.org/10.1016/j.molcata.2016.07.018

Lerari, D., & Benaboura, A. (2015). Preparation method effect on thermal properties of PMMA/Clay nanocomposite. *Mor. J. Chem.*, *3*(2), 202-211. https://doi.org/10.48317/IMIST.PRSM/morjchem-v3i2.2487

Maggi, L., Bruni, G., Ferrara, C., Puscalau, C., Quinzeni, I., Friuli, V., Monteforte, F., & Capsoni, D. (2023). Zaltoprofen-layered double hydroxide hybrids to enhance zaltoprofen solubility and dissolution rate. *Appl. Clay Sci.*, *231*. https://doi.org/10.1016/j.clay.2022.106723

Men, Y., Fang, X., Gu, Q., Singh, R., Wu, F., Danaci, D., Zhao, Q., Xiao, P., & Webley, P. A. (2020). Synthesis of Ni5Ga3 catalyst by Hydrotalcite-like compound (HTlc) precursors for CO_2 hydrogenation to methanol. *Appl. Catal. B., 275*, 119067. https://doi.org/10.1016/j.apcatb.2020.119067

Miyata, S. (1975). The Syntheses of Hydrotalcite-Like Compounds and Their Structures and Physico-Chemical Properties I: The Systems Mg^{2+}-$A1^{3+}$-NO_3^-, Mg^{2+}-$A1^{3+}$-$C1^-$, Mg^{2+}-$A1^{3+}$-ClO_4^-, Ni^{2+}-$A1^{3+}$-$C1^-$ and Zn^{2+}-Al^{3+}-Cl^-. *Clays Clay Miner.*, *23,* 369-375.

Oestreicher, V., Jobbágy, M., & Regazzoni, A. E. (2014). Halide exchange on Mg(II)-Al(III) layered double hydroxides: Exploring affinities and electrostatic predictive models. *Langmuir*, *30* (28), 8408–8415. https://doi.org/10.1021/la5015187

Pavel, O. D., Stamate, A. E., Zăvoianu, R., Bucur, I. C., Bîrjega, R., Angelescu, E., & Pârvulescu, V. I. (2020). Mechano-chemical versus co-precipitation for the preparation of Y-modified LDHs for cyclohexene oxidation and Claisen-Schmidt condensations. *Appl Catal A-Gen.*, *605*. 117797. https://doi.org/10.1016/J.APCATA.2020.117797

Periyasamy, S., Gopalakannan, V., & Viswanathan, N. (2018). Enhanced Chromium Sorption and Quick Separation of Magnetic Hydrotalcite Anchored Biopolymeric Composites Using the Hydrothermal Method. *J. Chem. Eng. Data.*, *63* (5), 1286–1299. https://doi.org/10.1021/acs.jced.7b00906

Radha, A. V., Kamath, P. V., & Shivakumara, C. (2007). Conservation of order, disorder, and "crystallinity" during anion-exchange reactions among Layered Double Hydroxides (LDHs) of Zn with Al. J. *Phys. Chem. B.*, *111* (13), 3411–3418. https://doi.org/10.1021/jp0684170

Taher, T., Gusti Wibowo, Y., Maulana, S., Rahayu Palapa, N., Rianjanu, A., & Lesbani, A. (2023). Facile synthesis of biochar/layered double oxides composite by one-step calcination for enhanced carbon dioxide (CO_2) adsorption. *Mater. Lett., 338,* 134068-134071. https://doi.org/10.1016/j.matlet.2023.134068

Tsuchida, T., & Ichikawa, N. (1989). Mechanochemical phenomena of gibbsite, bayerite and boehmite by grinding. *React. Solid, 7*, 207-217.

Wihadi, M. N. K., Haioka, T., Kojima, T., López, X., Ueda, T., Sano, T., & Sadakane, M. (2022). Synthesis and Structural Characterization of Multi-Molybdenum-Substituted Preyssler-type Phosphotungstates. *Eur. J. Inorg. Chem.*, *2022*(36), e202200533. https://doi.org/https://doi.org/10.1002/ejic.202200533

Wihadi, M. N. K., Hayashi, A., Ozeki, T., Ichihashi, K., Ota, H., Fujibayashi, M., Nishihara, S., Inoue, K., Tsunoji, N., Sano, T., & Sadakane, M. (2020). Synthesis of preyssler-type phosphotungstate with sodium cation in the central cavity through migration of the Ion. *Bull. Chem. Soc. Jpn.*, *93*(3), 461–466. https://doi.org/10.1246/BCSJ.20190326

Wihadi, M. N. K., & Sadakane, M. (2020). Solid-State Ion Migration in the Preyssler-Type Phosphotungstate for the Preparation of the Dipotassium Cation-Encapsulated Derivative. *Z. Anorg. Allg. Chem.*, *646*(15), 1297–1302. https://doi.org/10.1002/zaac.202000217

Yang, P., Yu, J., Wang, Z., Liu, Q., Wu, T. (2004). Urea Method for the Synthesis of Hydrotalcites. *React. Kinet. Catal. Lett., 83* (2004) 275-282.