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Cite as: AIP Conference Proceedings **2242**, 040058 (2020); <https://doi.org/10.1063/5.0007984>  
Published Online: 01 June 2020

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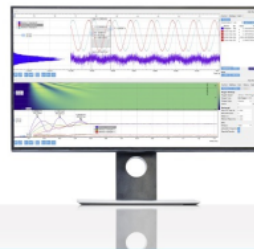
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# Thermal Reconstruction Properties of ZnFe LDH Prepared by Facile Hydrothermal Route

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**Abstract.** The thermal reconstruction properties of ZnFe LDH that prepared by a facile hydrothermal method has been investigated. The ZnFe LDH was synthesized by urea hydrolysis in hydrothermal condition with zinc nitrate and iron nitrate as the precursor. In order to investigate its thermal reconstruction properties, the obtained products were calcined at 600 °C followed by rehydration treatment under the presence of NO<sub>3</sub><sup>-</sup> ion solution. The properties of the natural, calcined, and reconstructed form of ZnFe LDH were investigated by X-ray diffraction, FT-IR, and TG-DTA analysis. The obtained result indicated that the calcined form of ZnFe LDH mainly composed of ZnO metal oxides. The calcined ZnFe LDH was successfully reconstructed.

**Keywords:** ZnFe LDH, thermal reconstruction, hydrothermal synthesis

## INTRODUCTION

Layered double hydroxides, familiar as hydrocalcite-like material or anionic clay, are 2D based layered material that has gained considerable attention in the last century, due to it exhibited potential applications in various fields like photocatalysis, catalyst, adsorbent, nanomedicine, composite material, etc. [1]. Furthermore, LDH has extensively explored owing to its unique physical and chemical properties such as layered structure, anion-exchange properties, water swelling, layered charge density and wide availability of chemical composition. The structure of the LDH layer was similar to brucite (Mg(OH)<sub>2</sub>), so then it also called as the brucite-like layer material. However, the LDH layer has a positive residual charge that emerged from the partial substitution of Mg<sup>2+</sup> by Al<sup>3+</sup> cation [2]. In general, the chemical formula of LDH can be presented as [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup> (A<sup>m-</sup>)<sub>x/m</sub>·nH<sub>2</sub>O, where M<sup>2+</sup> is a divalent metal cation while M<sup>3+</sup> is a trivalent [3]. A<sup>m-</sup> represents the interlayer species of the interlayer anion like CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> [4].

Theoretically, almost all types of anions might be intercalated inside the interlayer space of LDH [5]. Common anion groups that have been explored as intercalant agents including halides, oxoanion, oxometallate, anion complex, organic anion, and even anionic biomolecule [6-9]. Furthermore, a neutral molecule can also be inserted into the LDH structure. Hence, LDH not only has wide chemical composition but also broad in a variety of the interlayer species composition. Generally, the above-mentioned anion can be introduced into the LDH structure through ion exchange procedure [10]. However, in order to make sure that the insertion process is succeeded, the original interlayer anion that lies in the LDH structure should be weak enough to be changed by the target anion.

One of the parameters affecting the properties of LDH is the anion species that lies in the interlayer space of LDH. In order to produce an LDH material with good anionic properties, the interlayer anion species should be easily exchanged. Among the common LDH interlayer anion species, CO<sub>3</sub><sup>2-</sup> has reported as the hardest to get rid of [11].

Unfortunately, the presence of carbonate anion ( $\text{CO}_3^{2-}$ ) in the interlayer space of LDH is hardly avoided due to the capture of carbon dioxides in the atmosphere during the synthesis process. To overcome this problem, during the synthesis process, the surrounding synthesis environment must be free from any carbon dioxides. However, in some cases, that solution is hard to achieve.

In this work, an LDH material with Zn as  $\text{M}^{2+}$  metal ion and Fe as  $\text{M}^{3+}$  metal ion composition (ZnFe LDH), was synthesized by the facile urea hydrolysis method under hydrothermal condition. Due to the typical components of the obtained product was dominated by  $\text{CO}_3^{2-}$  anion, in this work the synthesized ZnFe LDH was further calcined at high temperature to remove the containing anions then followed by reconstruction (rehydration) under the presence of only  $\text{NO}_3^-$  anion.

## EXPERIMENTAL

### Materials

Zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was purchased from the Kanto chemical, Japan. Iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), and urea ( $\text{CH}_4\text{N}_2\text{O}$ ) were purchased from Wako Chemicals, Japan. All these mentioned chemicals were used as received without further purification for synthesizing the LDH material.

### Synthesis of ZnFe $\text{NO}_3$ LDH

The preparation of ZnFe LDH was conducted using facile urea hydrolysis in hydrothermal condition. In brief, 20 mmol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 10 mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved into 50 mL of distilled water consecutively under vigorous stirring for 10 min. In the other flask, 50 mmol of urea was dissolved into 30 mL of distilled water and stirred for further 10 min. The obtained mixed metal solution and urea solution were then transferred into 100 mL Teflon lined autoclave then moved into the laboratory oven for further heating at  $80^\circ\text{C}$  for 24 h. The obtained red-brown solid was then separated by vacuum filtration followed by rinsing with distilled water three times in order to remove the remaining metal salt solution. The washed solid was dried in a vacuum oven at  $80^\circ\text{C}$  for 8 h, and the obtained sample was then labeled as ZnFe LDH.

### Characterization

In this work, the prepared materials were characterized by X-ray diffraction analysis, FT-IR, and DTA analysis. The XRD analysis was conducted by using the XRD Rigaku SmartLab instrument at scanning range  $10^\circ$ – $80^\circ$ . The FT-IR analysis was conducted using FT-IR Jasco with KBr disk method at wavenumber range  $400$ – $4000\text{ cm}^{-1}$ . The differential thermal analysis (DTA) was carried out using a Shimadzu TG-DTA instrument under Nitrogen atmosphere at a temperature range of  $20$ – $900^\circ\text{C}$ .

## RESULTS AND DISCUSSION

XRD pattern of the as-synthesized ZnFe LDH, calcined ZnFe LDH at  $600^\circ\text{C}$  (labeled as ZnFe cal), reconstructed ZnFe cal (labeled as ZnFe rec) are presented in Fig. 1. The synthesized ZnFe LDH by the hydrothermal method showed a low crystallinity. However, several sharp peaks still can be recorded in the low diffraction angle that indicated the typical diffraction pattern of the LDH structure. The diffraction peak of (003) lattice plane that corresponds to the interlayer distance of the LDH was recorded at  $2\theta$  of  $11.18^\circ$  and the other typical diffraction of LDH can be observed at  $2\theta$  of  $28^\circ$ ,  $34^\circ$  and  $60^\circ$  [12]. The XRD pattern of the calcined ZnFe LDH showed that after it was calcined at  $600^\circ\text{C}$ , the typical diffraction pattern of LDH disappeared. Moreover, several new peaks observed at the diffraction pattern of the ZnFe cal. According to the JCPDS No. 36–1451, the sharp reflection peak located at  $32^\circ$ ,  $35^\circ$ ,  $36^\circ$ ,  $47^\circ$ ,  $56^\circ$  and  $62^\circ$  were corresponded to the (100), (002), (101), (102), (110) and (103) reflection peaks of ZnO [13]. This finding clearly indicated that after calcined at  $600^\circ\text{C}$ , the structure of ZnFe LDH was transformed into

its mixed metal oxides form. In order to investigate the memory effect properties of the ZnFe LDH, the ZnFe cal was further rehydrated under the existence of sodium nitrate solution. The diffraction pattern of the rehydrated ZnFe LDH can be shown in Fig. 1. It can be observed that the calcined ZnFe LDH in mixed metal oxides form can be reconstructed into its original LDH structure in which it can be identified from the sharp reflection peak at  $2\theta$  around  $12.6^\circ$  that corresponds to the typical (003) basal spacing of the LDH and the others characteristic peaks, i.e.  $34^\circ$ , and  $60^\circ$ . Moreover, the reconstructed ZnFe LDH exhibited much better crystallinity compared to its original form. These obtained results strongly indicated that ZnFe LDH that synthesized by urea hydrolysis method under hydrothermal condition has excellent memory effect properties.

FT-IR analysis was carried out on the prepared samples including ZnFe LDH, ZnFe Cal, and ZnFe Rec in order to investigate the interlayer composition and the function group. The FT-IR spectra of the prepared samples are presented in Fig. 2. As can be seen in that figure, the spectra of original ZnFe LDH exhibited characteristic vibration peaks of LDH in which the typical vibration of the interlayer water molecule and the surface hydroxyl group were recorded at a wavenumber of  $3453\text{ cm}^{-1}$  and  $1632\text{ cm}^{-1}$  [14]. Moreover, the interlayer anion that lied in the interlayer space of the LDH ( $\text{NO}_3^-/\text{CO}_3^{2-}$ ) can be identified as a sharp peak that emerged at wavenumber around  $1508\text{ cm}^{-1}$  and  $1384\text{ cm}^{-1}$  [15]. For the calcined ZnFe LDH, it was clearly exhibited that the vibration peaks that correspond to the interlayer water molecule and the interlayer anion drastically decreased. This finding indicated that the layered structure of the ZnFe LDH collapsed due to the removal of the interlayer species as induced by calcination at  $600^\circ\text{C}$ . Moreover, it can also be noticed that the typical vibration band of the metal-oxygen-Metal (M—O—M) bonding at wavenumber around  $1000\text{ cm}^{-1}$  removed after the calcination process [15]. It was an indication that the layered structure of the LDH was further transformed into mixed metal oxides form.

After rehydrated under the presence of  $\text{NO}_3^-$  anion, the FT-IR spectra of the reconstructed ZnFe LDH exhibited almost similar characteristics as the original ZnFe LDH. Moreover, it can be seen that the ZnFe rec showed a broader and higher intensity of the typical vibration band of the interlayer species at wavenumber around  $3400\text{ cm}^{-1}$  and  $1361\text{ cm}^{-1}$ . This finding exhibited that the reconstruction process was successfully conducted. Furthermore, it also can be observed that the vibration band that corresponds to the presence of  $\text{CO}_3^{2-}$  anion disappeared in the FT-IR spectra of the reconstructed ZnFe LDH. This phenomenon indicated the interlayer anion of the reconstructed ZnFe LDH was dominated by  $\text{NO}_3^-$  since it was introduced in the rehydration process.

Next, in order to further studying the composition of the prepared material, DTA analysis was further carried out. The results of this analysis are shown in Fig. 3. Although LDH has diverse composition, basically LDH exhibited almost similar thermal decomposition behavior upon heating. The interlayer water in the LDH structure released when heated up to ca.  $250^\circ\text{C}$  then followed by the decomposition of the interlayer anion species at the higher temperature (ca.  $250\text{--}400^\circ\text{C}$ ) [16]. As can be seen in Fig. 3, the DTA profile of the synthesized ZnFe LDH exhibited two main endothermic peaks observed at  $100^\circ\text{C}$  and  $200^\circ\text{C}$ . The first endothermic peak corresponds to the release of the interlayer water molecule while the second endothermic peak corresponds to the decomposition of the interlayer anion [17].

The DTA profile of the calcined ZnFe LDH did not show the typical DTA profile of the LDH. There are no endothermic peaks observed at the range temperature of  $100^\circ\text{C}$  to  $400^\circ\text{C}$  that indicated the absence of the water

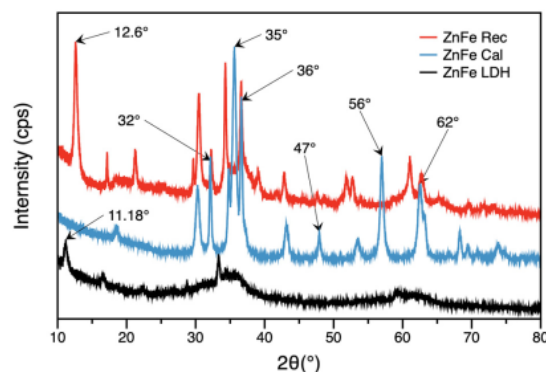
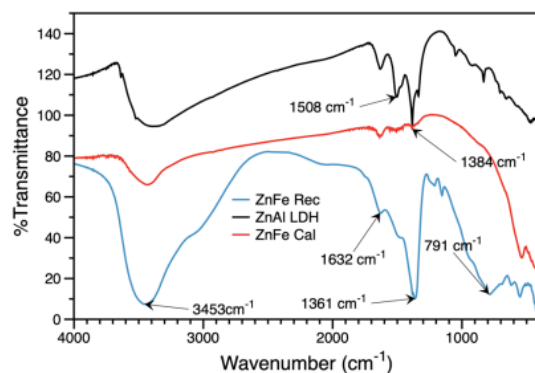
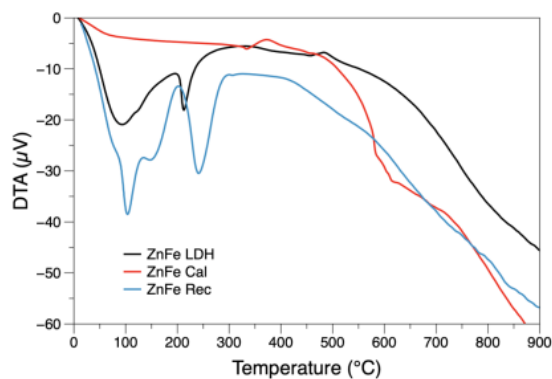


FIGURE 1. XRD pattern of the ZnFe LDH, ZnFe cal, ZnFe rec.



**FIGURE 2.** FT-IR spectra of ZnFe LDH, ZnFe cal, ZnFe rec.



**FIGURE 3.** DTA profile of ZnFe LDH, ZnFe cal, and ZnFe rec.

molecule and interlayer anion species. This finding is in agreement with the preceding discussion that indicated the collapse of the LDH interlayer structure. Moreover, the reconstructed ZnFe LDH showed almost a similar DTA profile as the original ZnFe LDH in which two endothermic peaks can be observed again. This finding clearly informs that the calcined ZnFe LDH could be transformed into its original form after rehydration process.

## CONCLUSION

In this work, ZnFe LDH was successfully synthesized by the facile hydrothermal method. The obtained material can be fully transformed into its mixed metal oxides (MMO) form by calcination at 600 °C. Moreover, the calcined ZnFe LDH in mixed metal oxide form can be reconstructed by rehydration under the presence of  $\text{NO}_3^-$  anion to form ZnFe- $\text{NO}_3$  LDH.

## ACKNOWLEDGMENTS

The authors sincerely thank the Ministry of Research, Technology, and Higher Education (Kemenristek Dikti) of Republik Indonesia for supporting this research through PMDSU scholarship batch II and PKPI scholarship 2018. This research also fully supported by the Institute of Regional Innovation (IRI), Hiroasaki University, Japan.

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