STUDY OF THERMAL DIFFUSIVITY OF Zn/Al LAYERED DOUBLE HYDROXIDE SYNTHESIZED WITH DIFFERENT MOLAR RATIO OF Zn/Al SALTS

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Thermal diffusivity of zinc-aluminum layered double hydroxides synthesized at different molar ratios of Zn to Al; at pH 7, 8 and 10 were measured using polyvinlidene diflouride (PVDF) photoflash technique. The samples were prepared using Zn $(NO_3)_2$ and Al $(NO_3)_3$ solutions by dropwise addition of NaOH solution with vigorous stirring under nitrogen atmosphere. The different ratios of Zn to Al were obtained by changing the molar ratio of Zn $(NO_3)_2$ to Al $(NO_3)_3$ solutions. The slurry formed was kept at 70 °C in an oil bath shaker for 18 h and then filtered, washed and dried in an oven for another 48 h at 70 °C. A simple photoflash and PVDF transducer were used as light source and thermal wave detector, respectively. All the measurements of thermal diffusivity of Zn-Al layered double hydroxide were carried out at room temperature. Thermal diffusivity for all series of sample prepared at pH=7, 8 and 10 increase from R=3 to R=5. Thermal diffusivity values of zinc-aluminum layered doubled hydroxide synthesized at pH 8 are higher than the values obtained for samples prepared at pH=7 (except for R=5) and at pH 10 are highest than two other series at pH 7 and 8.

1. Introduction

Thermal diffusivity is a basic thermal property of materials and its accurate value is often needed in many branches of physics and chemistry. Although numerous methods for measuring the thermal diffusivity of solid samples are exist such as laser flash [1], 3D-flash [2] heat pulse method [3] but the photo–flash technique was found to be the easiest, cheaper and simplest method for determining thermal diffusivity of solid samples [4, 5].

Inorganic–organic nanocomposite materials with functional organic compounds immobilized into a layered inorganic matrix have potential to offer scientific and technological advantages, since the organized two-dimensional arrays of organic species between the interlayers can result in novel functions that are different to the typical functions of the individual organic species [6–14].

An electrostatic layer-by-layer assembly technique that employs inorganic nanocomposites as building blocks is a possible means of forming a well-ordered multilayered architecture containing the arrays, because the nanocomposites have ultimate two-dimensional anisotropy with nanoscale thickness and microscale length in the plane of sheet [15]. It is known that some smectite clay minerals like montmorillonite, metal phosphates and layered oxides can be

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exfoliated into negatively charged nanosheets [16]. In contrast, positively charged nanosheets are a minority among exfoliated nanosheets. Recently, the exfoliation of layered double hydroxides (LDHs) has been studied as a method of preparing such positively charged nanosheets [17]. LDH nanosheets have high potential for use as building blocks to integrate negatively charged organic molecules into restricted arrays, due to their high stability and compatibility with many functional molecules [18–21].

Layered double hydroxide (LDH) is one of the attractive choices as nano-filler which have significantly improved the physicochemical properties of polymer matrix. In contrast to either neat polymer or the conventional composites, polymer nanocomposites are characterized by improved mechanical, thermal and barrier properties, reduced gas permeability, and flame retardancy [22–25]. Improvement in properties of the nanocomposites is related to their unique phase morphology that maximizes the interfacial interaction between the well-dispersed nanometer size domains and the matrices. LDH has received world-wide attention because they are useful to be incorporated in many applications, such as catalysis, stabilizer, flame retardant materials, medical materials, adsorbents, ion-exchangers, and in environmental chemistry [26].

The zinc-aluminum layered double hydroxide sample was chosen because it has many applications, such as flame retardant that can be used to enhance the properties of polymers. It is reported that LDHs contribute to the flame retardancy of the polymeric matrix, producing a refractory oxide residue on the surface of the material and releasing aqueous vapor and carbon dioxide during the decomposition. The endothermic nature of these processes and the dilution of combustible gases of pyrolysis increase the ignition time and reduce the heat release during the combustion [27–29].

The aim of this paper is to report the thermal diffusivity measurement of LDH using a simple polyvinlidene difluoride (PVDF) photo-thermal technique. In this research the preparation of Zn_3Al LDH nanocomposites is discussed. The morphological and thermal diffusivity properties of nanocomposites have been examined at various ratios (R) of Zn/Al for three pH values (i.e., 7, 8 and 10).

2. Experimental

A schematic diagram of the experimental setup is presented in Fig. 1. The system consists of a photoflash as a heating source and a film as a sensitive photothermal sensor. Avulcanized rubber was used as a backing material, and the sample was attached to the PVDF film using a thin layer of grease. The PVDF film thickness was 52 μm with the dimension of (12×30) mm^2. The photoflash was fixed at a position 3 cm from the sample surface and pulse duration was 5 ms. The photo-thermal signal was captured using a digital oscilloscope (Le Croy 9310A) equipped with averaging facilities. The experimental data was then plotted using software where the fitting procedure has been carried out based on the squared pulse approximation [30].

Three series of Zn-Al-LDH samples were synthesized by spontaneous self-assembly method of mixed aqueous solutions of $Zn(NO_3)_2$ and $Al(NO_3)_3$ at various molar ratios of Zn/Al (i.e., 2, 3, 4, 5 and 6). The first series of solution was maintained at pH=7 while the next series were kept at pH 8 and 10 respectively. The pH value was controlled by dropwise additions of NaOH solution under nitrogen atmosphere. The precipitate formed was aged at 70 °C in an oil bath shaker for 18 hours. The solution was then centrifuged and washed several times with decarbonated water and dried in an oven at 70 °C for 48 hours [7, 31, 32]. The particle size was in the range of (50–75) μm. The resulting LDH sample was grounded into fine powder and pressed to be a pellet form with 1.3 cm diameters and 1 mm thickness using a hydraulic pressing machine (Cover model 4350.L) for 10 minutes for thermal diffusivity measurements.

A Shimadzu XRD 6000 diffractometer with nickel filtered Cu-Kα (λ = 0.1542 nm) beam operated at 30 kV and 30 mA was used to determine the spacing of the Zn-Al-LDH, and ZnO composites using Bragg's equation $n\lambda = 2dsin\theta$. Data were recorded in 2θ range of 2°–60° using the scan rate of 2°/min.

The scanning electron micrographs of tensile fracture surface of the samples were recorded by a JSM-6400 scanning microscope which is a state-of-the-art high resolution scanning electron microscope with a modern digital image processing system. This SEM Joel operated at 20

kV to investigate the surface morphology of samples. The samples were coated with gold by a Bio-rad coating system before viewing. The scanning electron micrographs were recorded at the magnification of 2500X.
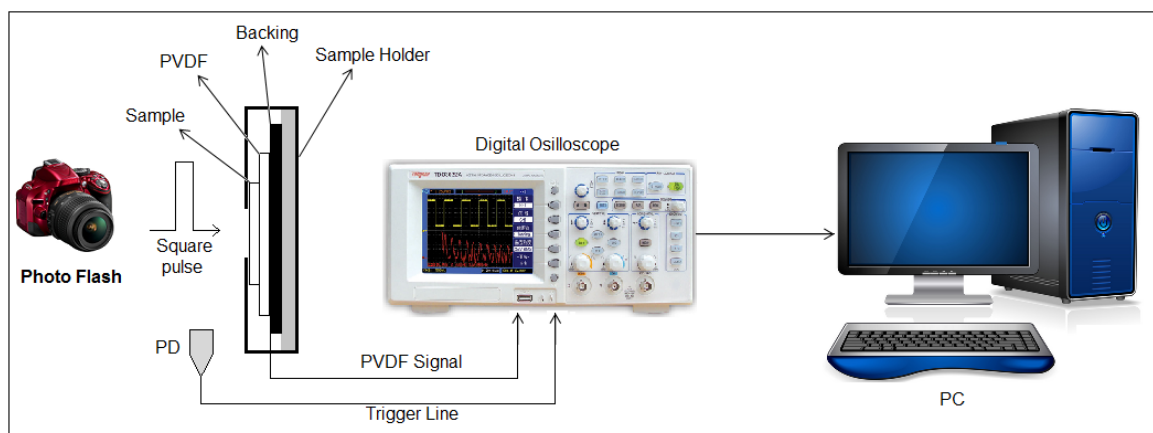

Fig. 1. The schematic diagram of the experimental setup.

3. Results and discussion

Figs. 2, 3 and 4 are the X-ray diffraction patterns obtained for samples prepared at pH 7, 8 and 10 where the ratio varied from R=2 to 6. The peaks appear around $30° < 2\theta < 37°$ are due to ZnO peaks. The ZnO peaks for pH 7 are observed for R= 4, 5 and 6; for pH 8 are observed for R= 3, 4, 5 and 6 and for pH 10 are observed for all ratios. This results shown that with the increases pH in the Zn-Al-LDH synthesized the ZnO preparation increases and also with the increases of molar ratios of Zn/Al salts, these three peaks intensity increases again.
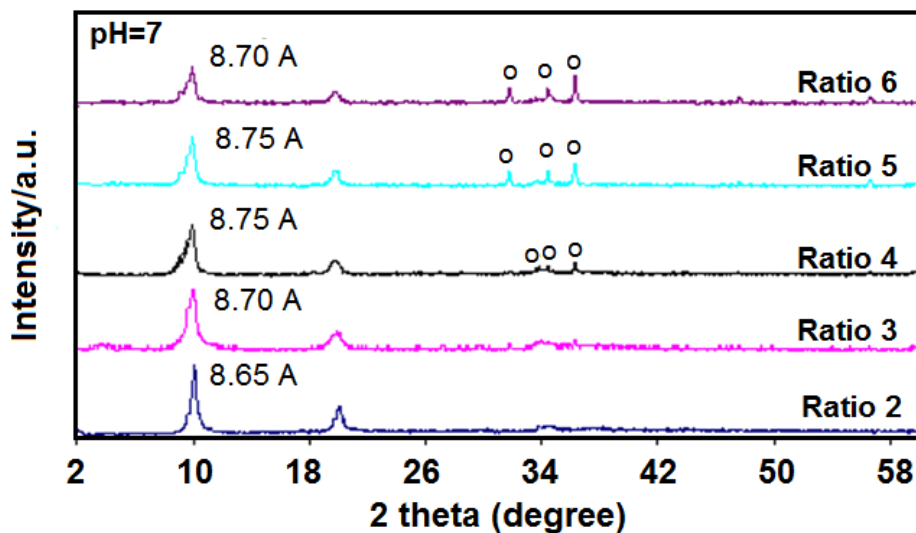

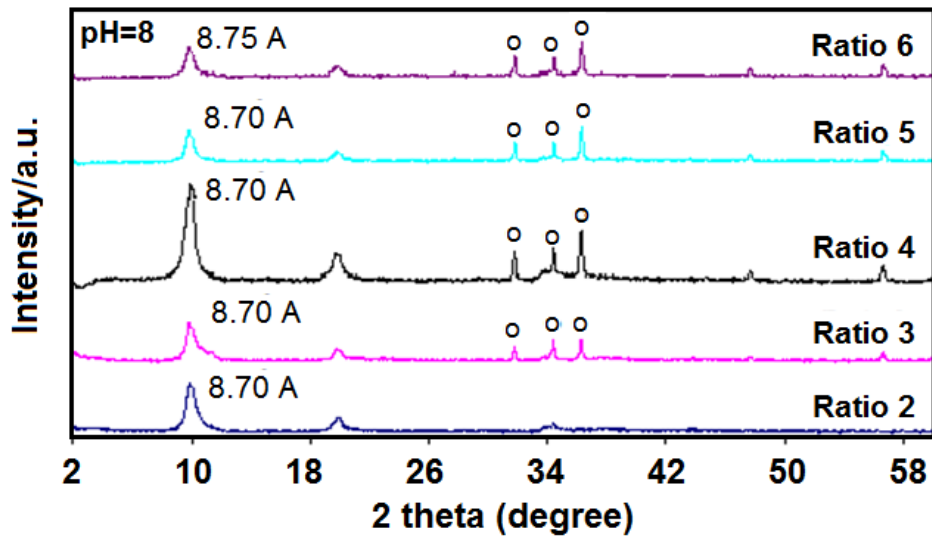*Fig. 2. X-ray diffractions of Zn-Al-LDH synthesized at pH 7 for Zn/Al ratio 2 to 6.*

Fig. 3. X-ray diffractions of Zn-Al-LDH synthesized at pH 8 for Zn/Al ratio 2 to 6.

The LDH peaks appeared at around $2\theta=10°$ with the basal spacing value ranging from 8.65 A to 8.80 A for all series of samples. The peak intensity decreases with the increasing of the Zn/Al ratio for samples prepared at pH 7. While for samples prepared at pH 8 and 10 the maximum peak appeared for Zn/Al ratio of 4.

Thermal diffusivity of zinc-aluminum layered double hydroxide was studied at different molar ratios of Zn/Al prepared at pH 7 and 8 using PVDF-photoflash technique. Fig. 5 shows a typical normalized photoflash signal detected by PVDF sensor. The solid line indicates the fitting line based on theoretical model developed by hydari 2004 [33-36].
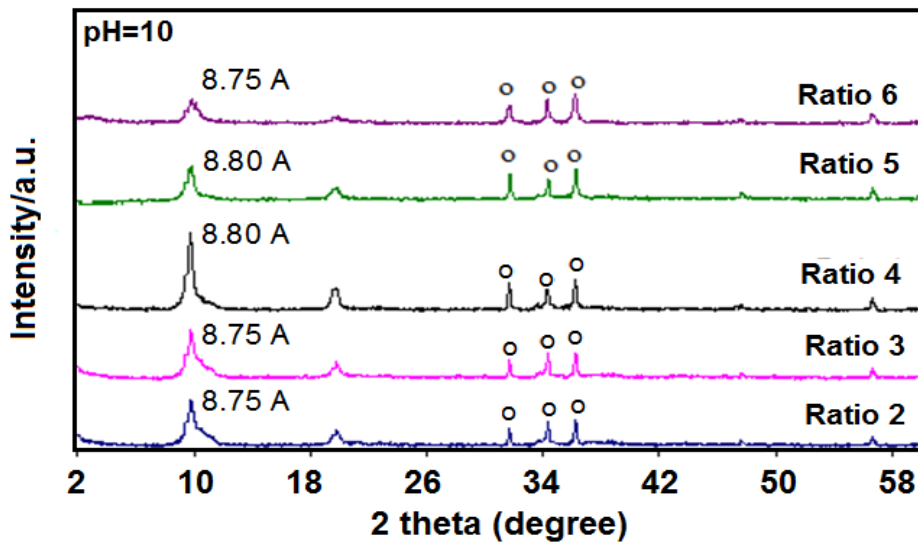

Fig. 4. X-ray diffractions of Zn-Al-LDH synthesized at pH 10 for Zn/Al ratio 2 to 6.

By considering one dimensional arrangement, the photo-thermal signal detected by PVDF sensor is given by below equation (1).

$$S(t) = \left(\frac{pd}{\varepsilon}\right)\frac{\partial}{\partial t} < \Delta t\, (x, t) >$$

(1)

Where d is the thickness of the pyroelectric detecting element, ε is its dielectric constant and $< \Delta (x, t) >$ is its spatially averaged temperature at position x and time t after absorption of light by sample's surface. The parameter p is the pyroelectric coefficient of the device, which indicates the extent of the change in polarisation per unit change in the temperature [30]. Thus, fitting the

experimental data to the theoretical formulation produced the thermal diffusivity values of the samples.
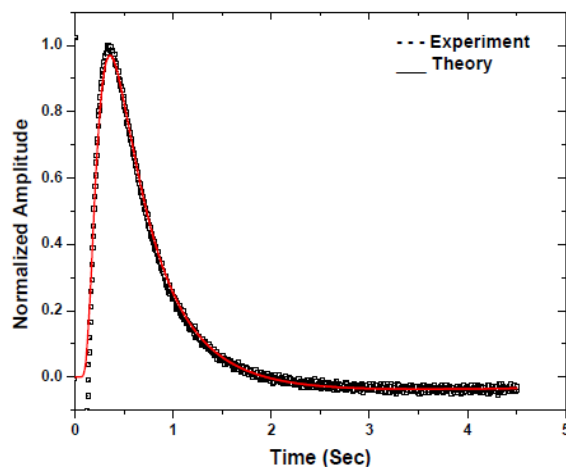

Fig. 5. PVDF response from Zn-Al-LDH sample (square).
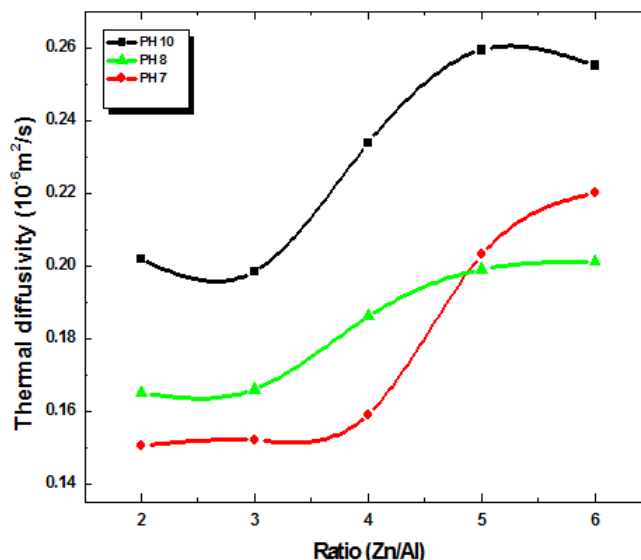*The solid line is theoretically calculated data.*

Fig. 6. Thermal diffusivity (α) of Zn-Al-LDH as a function of Zn/Al molar ratio.

The variations of thermal diffusivity as a function of Zn/Al ratio for three series of Zn-Al-LDH samples are shown in Fig.6. For all three series samples the thermal diffusivity increases with the increasing of Zn/Al ratio where samples prepared at pH 8 higher than the sample at pH7 (except for R = 5) and pH 10 shows higher than pH 8.

Also the surface morphology (SEM) of Zn-Al-LDH synthesized at various pHs of 7, 8 and 10 obtained by a scanning electron microscope and are shown in Figs. 7, 8 and 9 for ratio 4, respectively. As shown in SEM results the crystallinity and porosity of samples in the pH=7 to 8 and 10 gradually increases. Moreover, the ZnO crystal structure in the Zn-Al-LDH layers formed and completed. These results confirmed with XRD results appear around $30° < 2\theta < 37°$ that are due to ZnO peaks and also the intensity of peaks increases gradually.
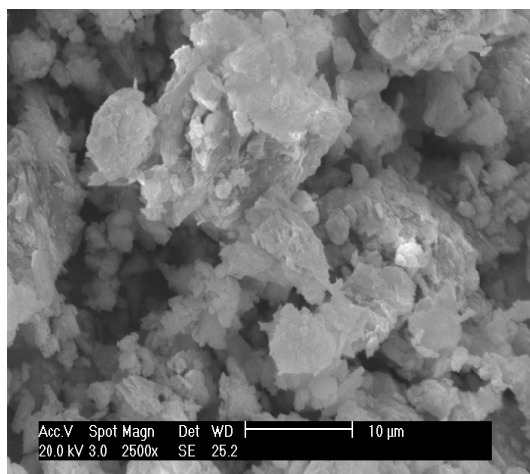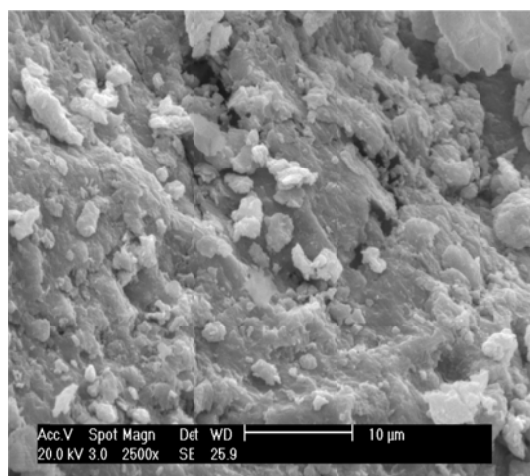
Fig. 7. Surface morphology of Zn-Al-LDH prepared at pH 7.

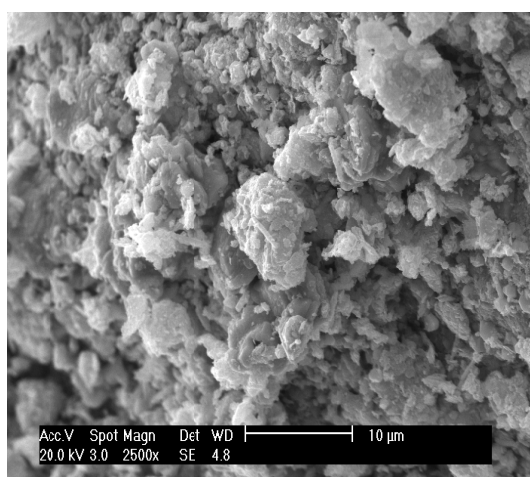*Fig. 8. Surface morphology of Zn-Al-LDH prepared at pH 8.*

Fig. 9. Surface morphology of Zn-Al-LDH prepared at pH 10.

4. Conclusions

Thermal diffusivity of Zn-Al-LDH as a function of Zn/Al ratio has been successfully measured using PVDF photoflash technique. The pH and the molar ratio of Zn/Al are the

important parameters to control the thermal diffusivity of the LDH sample. Thermal diffusivity of Zn-Al-LDH prepared at pH 10 was highest than the samples prepared at pH 7 and pH 8. The crystallinity and porosity of samples in pH 10 are complete according to XRD and SEM results.

Acknowledgements

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