UNIVERSITI PUTRA MALAYSIA

THERMAL DIFFUSIVITY OF ZINC ALUMINUM – LAYERED DOUBLE HYDROXIDE USING PHOTOFLASH TECHNIQUE

MARYAM RANJBAR GHAZIEAN

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By

MARYAM RANJBAR GHAZEIAN

Thesis submitted to the School of Graduate Studied, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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DEDICATION

To my beloved parents Sedigheh and Fereydon for their love and concern

To my friend Reza Meimandi Parizi for his support and encouragement

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

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Chair: Professor W.Mahmood Mat Yunus, PhD

Faculty: Science

Thermal diffusivity of zinc aluminum layered double hydroxide (Zn-Al-LDH) was measured by using photoflash technique. It used a simple camera flash and polyvinlidene diflouride (PVDF) film as signal generating source and detector respectively.

Three series of sample were prepared at pH 7, 8 and 10 and with molar ratios of Zn to Al in a range from 2 to 6 (Zn/Al = 2, 3, 4, 5 and 6).

The ZnO peaks appeared in x-ray diffraction pattern for all samples except for samples prepared at pH 7 with ratio 2 and 3 (Zn/Al = 2 and 3) and sample prepared at pH 8 with ratio 4. The ZnO peaks observed were between $2\theta = 30^\circ$ to $2\theta = 37^\circ$.

Thermal diffusivity for all three series samples (pHs 7, 8 and 10) was measured at room temperature. The thermal diffusivity for all three series of samples was found to increase for the case of molar ratio 2 to 6.

The thermal diffusivity for Zn-Al-LDH at different ratios of Zn-Al-LDH increased with increasing ratio of Zn to Al. The increasing of thermal diffusivity is due to increasing of ZnO. Thermal diffusivity at pH 7, increased from $0.15\times10^{-6} m^2/s$ to $0.22\times10^{-6} m^2/s$. Thermal diffusivity of sample prepared at pH 8 increased from $0.16\times10^{-6} m^2/s$ to $0.20\times10^{-6} m^2/s$ while at pH 10, if increased from $0.20\times10^{-6} m^2/s$ to $0.25\times10^{-6} m^2/s$. Thermal diffusivity at pH 7 has the lowest value and at pH 10 has the highest value.

The sample prepared at pH 7 with ratio 4 (Zn/Al = 4) was heat-treated at different temperature from 200˚C to 600˚C, prior to thermal diffusivity measurement at room temperature.

In the case of heat treated samples, the thermal diffusivity increased from $0.25\times10^{-6} m^2/s$ to $0.40\times10^{-6} m^2/s$ with increasing treatment temperature.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGUKURAN PERESAPAN TERMA UNTUK LAPISAN ZINK ALUMINIUM BERGANDA HYDROSIDA MENGGUNAKAN TEKNIK FOTO-KILAT

Oleh

MARYAM RANJBAR GHAZIEAN

February 2009

Pengerusi: Profesor W.Mahmood Mat Yunus, PhD

Fakulti: Sains

Peresapan terma untuk hidroksida berlapis ganda Zink-Aluminum (Zn-Al-LDH) telah diukur menggunakan teknik foto-kilat. Ianya menggunakan cahaya kilat daripada kamera biasa digunakan sebagai sumber isyarat dan filem polyvinlidene diflouride (PVDF) pengesan. Tiga siri sampel disediakan pada pH7, 8, dan 10. Setiap siri mempunyai molar yang berbeza dengan nisbah Zn kepada Al, dalam julat daripada 2 hingga 6 (Zn/Al = 2, 3, 4, 5 dan 6). Puncak-puncak terhasil dalam corak pembelauan sinar-x bagi ZnO untuk semua sampel kecuali bagi sampel yang disediakan pada pH7 dengan molar 2 dan 3 (Zn/Al = 2 dan 3) dan sampel yang disediakan pada pH8 dengan nisbah Zn/Al = 4. Puncak ZnO telah dapat dilihat pada $2\theta = 30^{\circ}$ hingga $2\theta = 37^{\circ}$.

Peresapan terma untuk ketiga-tiga siri sampel (pH 7, 8 dan 10) telah diukur pada suhu

bilik. Peresapan terma bagi ketiga-tiga sampel telah didapati meningkat untuk kes yang molarnya 2 hingga 6. Peresapan terma untuk Zn-Al-LDH dengan pada nisbah Zn/Al yang berbeza dengan peningkatan nisbah Zn kepada Al. Peningkatan peresapan terma adalah disebabkan oleh peningkatan ZnO. Peresapan terma pada pH7, meningkat daripada $0.15\times10^{-6}m^2/s$ kepada $0.22\times10^{-6}m^2/s$. Peresapan terma bagi sampel yang disediakan pada pH8 meningkat daripada $0.16\times10^{-6}m^2/s$ kepada $0.20\times10^{-6}m^2/s$ manakala bnpada pH10 pula meningkat daripada $0.20\times10^{-6}m^2/s$ kepada $0.25\times10^{-6}m^2/s$. Peresapan terma pada pH7 adalah merupakan nilai peresapan terma yang terendah dan pH10 adalah merupakan yang tertinggi.

Sampel yang disediakan pada pH7 dengan nisbah (Zn/Al = 4) telah diberikan rawatan haba pada suhu yang berbeza-beza daripada 200˚C kepada 600˚C, keutamaan untuk pengukuran peresapan terma pada suhu bilik. Dalam kes sampel yang telah dirawat oleh suhu, peresapan terma telah meningkat daripada $0.25\times10^{-6}m^2/s$ kepada $0.40\times10^{-6}m^2/s$ dengan peningkatan perawatan suhu.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were follows:

W. Mahmood Mat Yunus, PhD.
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Maarof Moksin, PhD.
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohd Zobir Hussein, PhD.
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

HASANAH MOHD. GHAZALI, PhD
Professor and Dean
School of Graduate
Universiti Putra Malaysia

Date: 9 April 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that is has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Maryam Ranjbar

Date:

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LIST OF ABBREVIATION

Å	Angstrom
PVDF	Polyvinlidene Difluoride
LDH	layered double hydroxide
PXRD	powder x-ray diffraction
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
CHN	carbon, hydrogen and nitrogen
IR	Infrared characterization
HTLc	hydrotalcite -like compound
OTTER	optothermal transient emission radiometry
Zn-Al-LDH	Zinc Aluminum layered double hydroxide
R	Ratio
N.A	normalized amplitude
L	Thickness of sample
K	Kelvin temperature
YBCO	Y-Ba-Cu-O system
CPC	closed photoacoustic cell
OPC	open photoacoustic cell
BSCCO	Bi-Sr-Ca-Cu-O system

LIST OF SYMBOLS

k	Thermal conductivity
α	Thermal diffusivity
θ	angle between the incident ray the scattering planes
d	diameter of the sample
$Al(NO_3)_2$	Aluminum nitrate
$Zn(NO_3)_2$	Zinc nitrate
λ	wavelength of x-ray diffraction
d	spacing between the planes
l	sample thickness
$(NO_3)^-$	Nitrate
ρ	density
c	Specific heat
V	Voltage
T	Time
f	Frequency
I	Current
∇	Gradient transverse
Q	quantity of heat

CHAPTER 1

INTRODUCTION

Thermal diffusivity is one of the most important physical properties of materials that present thermal behavior in the materials. Thermal diffusivity is also one of the most important thermal properties of the photonic and electronic devices. One of the general methods for measurement of thermal diffusivity is the flash method (Parker et al., 1961). The flash method uses a short light pulse to dissipate heat on front surface of the sample. The temperature on the rear surface of the sample is monitored and thermal diffusivity can be calculated by analyzing the temperature profile of the back sample.

For the steady – state conditions, the rate of heat diffusion can be written in Fourier – Biot equation:

$$\frac{Q}{A} = k \left(\frac{\partial T}{\partial x} \right) \tag{1.1}$$

In equation (1.1) Q is the quantity of heat flowing in a unit time through an area A under the temperature gradient $\frac{\partial T}{\partial x}$ and k is the thermal conductivity.

When thermal properties of materials are independent of temperature but the temperature varies with time (t), equation (1.1) becomes:

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \qquad (1.2)$$

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial x^2} \qquad (1.3)$$

where ρ is the density of Zinc-Aluminum-layered double hydroxide and C_p is the specific heat at constant pressure.

Thus $$\frac{k}{\rho C_p} = \alpha \qquad (1.4)$$

where α is the thermal diffusivity of the substance.

In the late 1990′s, the thermal diffusivity was measured quantitatively with the delicate experiment device and the raw data processing (Bennis et al., 1998; Ogawa et al., 1999). After the year 2000 the measurement was focused on the application of various types of materials and solids. It is important to measure thermal properties and thermal behavior of various types of materials such as liquid, gas and solid materials (metals, nonmetals, semiconductors, bi-layer materials and thin film (Kim et al., 2007). Because thermal properties were used to search the specialty of heat transfer for the materials, which have a microstructure or nanostructure.

Thermal diffusivity is the quantity related to the propagation of heat. Many photothermal techniques have been used to measure thermal diffusivity of solids, liquid and gas.

1.1 Photothermal Technique

One of the most popular methods used for measuring thermal diffusivity is the flash method (Kim et al., 2007). In this technique a pulse of light such as a flash lamp, camera flash or laser is irradiated on the surface of the sample. The effect of this radiation absorption produces a heat called "thermal wave". By using photothermal method identification of the materials through its properties is made possible (Haydari, 2004).

There are two ways for detecting thermal wave: direct and indirect detection. The direct way such as thermocouple detection and pyroelectric, while indirect detection such as photoacoustic technique and thermal lens.

1.1.1 Photoflash Technique

Photoflash technique is one of the varieties of photothermal techniques, which based on the thermal wave detection due to modulated light absorption in the materials. The set up with a short light pulse diffuse on the surface of the sample. Then the temperature in the back of the sample increased. There is a PVDF sensor in the rear of the sample. The temperature was detected using a PVDF, and then data were sent to the oscilloscope. Then the experimental data were fitted with theoretical model.

The heat has to travel from the front of the sample to the back of the sample, the effect of heat is loss especially when the sample is thicker or the thermal diffusivity of the sample is lower. When the sample has the right thickness the PVDF can detect the heat in the rear of the sample (Haydari, 2004).

1.2 Thermal Diffusivity of Solid

Thermal diffusivity is a parameter which determines the time dependent condition for unsteady state. It provides both direct and indirect information for materials of industrial interest. The first exact formula for hydrotalcite was $[Mg_6Al_2(OH)_{16}CO_3.4H_2O]$. Hydrotalcite is a mineral that can be easily crushed into a white powder similar to talc. Around 1842 in Sweden, LDH was discovered, also at the same time another compound of hydroxycarbonate magnesium and iron was discovered which called pyroaurite because was similar to gold materials when it was heated. Later on isostructural was discovered with hydrotalcite similar layered double hydroxide as having similar features (Cavani et al., 1991).

The extensive work on physico-chemical characterization of the hydrotalcites is the reason why hydrotalcite is used as reference name in many applications. Also the preparation of hydrotalcites in laboratory is simple and relatively inexpensive. To the best of our knowledge, there is no complete report on thermal diffusivity of zinc - aluminum - layered double hydroxide. For these reasons we have focus this study on investigating the thermal diffusivity of zinc - aluminum - layered double hydroxide was measured at room temperature with different ratios of Zn to Al molar and different pH. Also the thermal diffusivity of Zn-Al-LDH was measured for pH 7 after heat –treated the sample in an electronic furnace at different temperature from 200˚C to 600˚C.

1.3 Thermal Carriers in Solids

The heat is transferred from a point to another point via conduction, convection or radiation. Normally in solid material, the heat is transferred via conduction. In solid materials with high porosity, the heat can be transferred across a pore by convection and radiation as well as conduction. There are three classes for solid materials; metals, insulators and semiconductors. In metals, the free electrons are so many and the thermal energy is transferred by electrons. In insulator, the free electrons are so few and in semiconductors phonons and electrons are equally important as carries of thermal energy.

1.4 Zinc Oxide

Zinc oxide is one of the most important chemical compounds with the formula written as ZnO (Figure 1.1). It is insoluble in water but soluble in acids. The color of zinc oxide powder is white. As a mineral was found in nature but the crystal form of zinc oxide is rare (Suzuki et al., 1988). The crystalline of zinc oxide produces the piezoelectric effect and is thermochromic (ability of substance to change color). The crystalline of zinc oxide is able to change from white color to yellow when heated. ZnO is a semiconductor