

**THE UV-SHIELDING PROPERTY OF
 $Zr_{0.7}Ce_{0.3}O_2$ -KAOLINITE/EXFOLIATED KAOLINITE
COMPOSITES PREPARED BY DIFFERENTSYNTHESIS
METHODS**

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**UNIVERSITI SAINS MALAYSIA
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by

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LIST OF ABBREVIATIONS

| | |
|-----------------------------|--|
| 1,25[OH]D | 1,25-dihydroxyvitamine D3 |
| AD | Anno Domini |
| BC | Before Christ |
| BCE | Before the Christian Era |
| BET | Brunauer–Emmett–Teller |
| CDC | Calcia-Doped Ceria |
| CEC | Cation Exchange Capacity |
| CeO ₂ (HT) | CeO ₂ prepared by hydrothermal treatment method without sodium oleated added |
| CeO ₂ (HTO) | CeO ₂ prepared by hydrothermal treatment method with sodium oleated added |
| CeO ₂ -500 (HTO) | CeO ₂ prepared by hydrothermal treatment method with sodium oleated added after calcination at 500 °C for 5 h |
| CMCs | Ceramic Matric Composites |
| CT | Citric acid complexing method without NH ₃ added |
| CT-NH ₃ | Citric acid method complexing with NH ₃ added |
| DMSO | Dimethylsulfoxide |
| DNA | Deoxyribonucleic Acid |
| EPMA | Electron Probe Microanalysis |
| ESEM | Environmental Scanning Electron Microscope |
| Ex | Exfoliated kaolinite |
| FESEM | Field Emission Scanning Electron Microscopy |
| FTIR | Fourier Transform Infrared Spectroscopy |

| | |
|-------------------|---|
| FWHM | Full Width at Half Maximum |
| HT | Hydrothermal Treatment method without sodium oleate added |
| HTO | Hydrothermal Treatment method with sodium oleate added |
| ICDD | International Centre for Diffraction Data |
| IR | Infrared |
| K | Kaolinite |
| KU1 | Urea-treated Kaolinite for 1 hour |
| KU3 | Urea-treated Kaolinite for 3 hours |
| KU5 | Urea-treated Kaolinite for 5 hours |
| LOI | Loss on Ignition |
| PLT | Plate-Like Titanate |
| PTFE | Polytetrafluoroethylene |
| SM | Solid Mixing |
| SSA | Specific Surface Area |
| SSC | Soft Solution Chemical method |
| TG/DTA | Thermogravimetry-Differential Thermal Analysis |
| T-O-T | Tetrahedral-Octahedral-Tetrahedral |
| U | Urea |
| UV | Ultraviolet |
| UV-Vis | Ultraviolet-Visible spectroscopy |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Fluorescence |
| ZCO | $Zr_{0.7}Ce_{0.3}O_2$ |
| ZCO _{CT} | $Zr_{0.7}Ce_{0.3}O_2$ prepared by a citric acid complexing method |

| | |
|------------------------------|---|
| ZCO _{CT} -Ex (SM) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by a solid mixing method |
| ZCO _{CT} -K (SM) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by a solid mixing method |
| ZCO-Ex (CT) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by a citric acid complexing method |
| ZCO-Ex (CT-NH ₃) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by a citric acid complexing method with NH ₃ added |
| ZCO-Ex (HT) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by hydrothermal treatment method without sodium oleate added |
| ZCO-Ex (HTO) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by hydrothermal treatment method with sodium oleate added |
| ZCO-Ex (SSC) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by a soft solution chemical method |
| ZCO-Ex | Zr _{0.7} Ce _{0.3} O ₂ -Exfoliated kaolinite composite |
| ZCO-Ex-500 (HTO) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by hydrothermal treatment method with sodium oleate added after calcination at 500 °C for 5 h |
| ZCO _{HT} | Zr _{0.7} Ce _{0.3} O ₂ prepared by a Hydrothermal Treatment method without sodium oleate added |
| ZCO _{HT} -Ex (SM) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by a solid mixing method |
| ZCO _{HT} -K (SM) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by a solid mixing method |

| | |
|-----------------------------|---|
| ZCO _{HTO} | Zr _{0.7} Ce _{0.3} O ₂ prepared by a Hydrothermal Treatment method with sodium oleate added before calcination at 500 °C |
| ZCO _{HTO} -500 | Zr _{0.7} Ce _{0.3} O ₂ prepared by a Hydrothermal Treatment method with sodium oleate added after calcination at 500 °C |
| ZCO-K (CT) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared a citric acid complexing method |
| ZCO-K (CT-NH ₃) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared a citric acid complexing method with NH ₃ added |
| ZCO-K (HT) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by hydrothermal treatment method without sodium oleated added |
| ZCO-K (HTO) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by hydrothermal treatment method with sodium oleated added |
| ZCO-K (SSC) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by a soft solution chemical method |
| ZCO-K | Zr _{0.7} Ce _{0.3} O ₂ -Kaolinite composite |
| ZCO-K-500 (HTO) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by hydrothermal treatment method with sodium oleated added after calcination at 500 °C for 5 h |
| ZCO _{SSC} | Zr _{0.7} Ce _{0.3} O ₂ prepared by a soft solution chemical method |
| ZCO _{SSC} -Ex (SM) | Zr _{0.7} Ce _{0.3} O ₂ -exfoliated kaolinite composite prepared by a solid mixing method |
| ZCO _{SSC} -K (SM) | Zr _{0.7} Ce _{0.3} O ₂ -kaolinite composite prepared by a solid mixing method |
| ZrO ₂ (HT) | ZrO ₂ prepared by hydrothermal treatment method without sodium oleated added |

| | |
|-----------------------------|--|
| ZrO ₂ (HTO) | ZrO ₂ prepared by hydrothermal treatment method with sodium oleated added |
| ZrO ₂ -500 (HTO) | ZrO ₂ prepared by hydrothermal treatment method with sodium oleated added after calcination at 500 °C for 5 h |

**SIFAT PELINDUNGAN UV KOMPOSIT $Zr_{0.7}Ce_{0.3}O_2$ -KAOLINIT/KAOLINIT
TERNYAHLAPIS YANG DISEDIAKAN MENERUSI KAEDAH SINTESIS
YANG BERBEZA**

ABSTRAK

Kaolinit telah diperolehi dengan pengelutritan sisa lombong, yang kemudiannya dinyahlapis dengan pengisar bebola planet menggunakan urea sebanyak 40 wt.% selama 1, 3 dan 5 jam. Seterusnya, sampel kaolinit dan kaolinit terawat urea ditentukan sifatnya menerusi XRD, XRF, SEM, FTIR, and BET. Keputusan bagi sampel kaolinit dan kaolinit terawat urea selama 1, 3 dan 5 jam mengesahkan bahawa kaolinit berjaya dinyahlapis melalui rawatan urea selama 5 jam dan keputusan XRD bagi kaolinit menunjukkan kehadiran kecil gipsit dan muskovit. Komposit $Zr_{0.7}Ce_{0.3}O_2$ -kaolinit/kaolinit ternyahlapis telah disediakan dengan tiga kaedah sintesis *in-situ* yang berbeza dan satu kaedah pencampuran pepejal. Kaedah sintesis *in-situ* yang pertama adalah kaedah pengkompleksan asid sitrik (dengan dan tanpa tambahan NH_3). Kedua, kaedah kimia larutan lembut; dan ketiga adalah kaedah rawatan hidroterma (dengan dan tanpa tambahan sodium oleat). Untuk kaedah pencampuran pepejal, $Zr_{0.7}Ce_{0.3}O_2$, yang disediakan menerusi tiga kaedah sintesis yang berbeza tersebut, telah dicampur dengan kaolinit/kaolinit ternyahlapis dengan menggunakan lesung dan alu agat. Komposit yang terhasil telah ditentukan sifatnya menerusi XRD, FESEM dan UV-Vis. Bagi komposit $Zr_{0.7}Ce_{0.3}O_2$ -kaolinit/kaolinit ternyahlapis, keputusan XRD bagi komposit yang disediakan dengan kaedah pencampuran pepejal menunjukkan puncak belauan mineral kaolinit. Walau bagaimanapun, bagi komposit yang disediakan dengan kaedah sintesis *in-situ*,

puncak belauan ini tidak wujud kerana kaolinit/kaolinit ternyahlapis telah terurai akibat pengkalsinan. Perbandingan sifat pelindungan UV bagi kesemua bahan komposit yang disediakan dengan menggunakan kaedah yang berbeza menunjukkan $Zr_{0.7}Ce_{0.3}O_2$ -kaolinit ternyahlapis yang disediakan menerusi kaedah pengkompleksan asid sitrik (tanpa NH_3) mempamerkan sifat pelindungan UV yang terbaik kerana kehadiran kaolinit ternyahlapis dalam komposit yang terserak secara seragam dan penyerapan UV yang baik oleh $Zr_{0.7}Ce_{0.3}O_2$ berbanding dengan bahan-bahan komposit yang lain. Tambahan pula, dengan mengubah kepekatan kaolinit ternyahlapis daripada 5 hingga 50 wt. %, keamatan puncak XRD $Zr_{0.7}Ce_{0.3}O_2$ berkurang kerana kepekatan kaolinit ternyahlapis meningkat. Komposit dengan 30 wt. % kaolinit ternyahlapis menghasilkan keupayaan menyerap UV yang terbaik manakala komposit dengan 40 wt. % kaolinit ternyahlapis menghasilkan keupayaan menyerap cahaya tampak yang terbaik.

**THE UV-SHIELDING PROPERTY OF $Zr_{0.7}Ce_{0.3}O_2$ -
KAOLINITE/EXFOLIATED KAOLINITE COMPOSITES PREPARED BY
DIFFERENT SYNTHESIS METHODS**

ABSTRACT

Kaolinite was obtained by elutriation of tin slime, which was then exfoliated by planetary ball milling with 40 wt. % of urea for 1, 3 and 5 hours. Then the kaolinite and urea-treated kaolinite samples were characterized by using XRD, XRF, SEM, FTIR, and BET. The characterization results of kaolinite and urea-treated kaolinite samples for 1, 3 and 5 hours proved that kaolinite was successfully exfoliated by urea treatment for 5 hours and the XRD result of kaolinite showed minor gibbsite and muscovite as impurities. Composites of $Zr_{0.7}Ce_{0.3}O_2$ -kaolinite/exfoliated kaolinite were prepared by three different *in-situ* synthesis methods and one solid mixing method. The first *in-situ* synthesis method was a citric acid complexing method, with and without NH_3 added; the second *in-situ* synthesis method was a soft solution chemical method; and the third *in-situ* synthesis method was a hydrothermal treatment method with and without sodium oleate added. For the solid mixing method, $Zr_{0.7}Ce_{0.3}O_2$, which was prepared by the three different synthesis methods such as a citric acid complexing method without NH_3 added, a soft solution chemical method and a hydrothermal treatment without sodium oleate added, was solid mixed with kaolinite/exfoliated kaolinite using an agate mortar and pestle. The resulting composites were characterized by using XRD, FESEM and UV-Vis. For $Zr_{0.7}Ce_{0.3}O_2$ -kaolinite/exfoliated kaolinite composites, the XRD patterns of the composites, which were prepared by solid mixing method, showed the reflection

peaks of kaolinite. However, for the composites which were prepared by *in-situ* synthesis methods, the reflection peaks of kaolinite were not visible as the kaolinite/exfoliated kaolinite structure collapsed during calcination. The comparison of the UV-shielding property of all the composite materials prepared by the different methods showed that $Zr_{0.7}Ce_{0.3}O_2$ -exfoliated kaolinite prepared by using the citric acid complexing method without NH_3 added has the best UV-shielding property as it possesses a well dispersed of exfoliated kaolinite in the composite and a good UV-absorption of $Zr_{0.7}Ce_{0.3}O_2$ compared to that of other composite materials. Furthermore, by changing the concentration of exfoliated kaolinite from 5 to 50 wt. %, the peaks intensities of $Zr_{0.7}Ce_{0.3}O_2$ were decreased as the concentration of exfoliated kaolinite was increased. The composite with 30 wt. % of exfoliated kaolinite produced the best UV-absorption ability whilst the composite with 40 wt. % of exfoliated kaolinite produced the best visible light absorption ability.

CHAPTER 1

INTRODUCTION

1.1 Background and problem statement

There have been considerable impacts on the concentration of ozone layer due to human activity on Earth and the changes in atmospheric composition. The thinning of the ozone layer results in increasing UV radiation dosage. Even a relatively small increase in UV radiation has a substantial impact on human skin and eyes, the biosphere, and the products of the ground-level ozone. UV exposure also leads to the development of skin cancers, including deadly melanomas, and perturbs the immune system of the body (Valášková et al., 2007).

UV is grouped into three types as UV-A, UV-B and UV-C based on their wavelength ranges, i.e. UV-A for 315-400 nm, UV-B for 280-315 nm and UV-C for 280-100 nm (Mackie, 2000). UV-C is part of natural sunlight, but filtered in the upper atmospheric horizon. However, UV-B and UV-A are known to have considerable influence. Between two to three million non-melanoma skin cancers and approximately 132,000 melanoma skin cancers occur globally each year whilst 12 to 15 million people are blind from cataracts. According to WHO (World Health Organization) estimates, more than 90 % of skin cancers and up to 20 % of blindness are caused by sun exposure (World.Health.Organization, 2002). Consequently, a great deal of recent research has focused on the development of photo-protective materials (Mackie, 2000; Valášková et al., 2007).

Many researchers have focused on the preparation of UV-shielding materials such as ZrO_2 , TiO_2 , ZnO , CeO_2 , $ZnO-ZrO_2$, ZrO_2-CeO_2 , CeO_2-CaO and $ZnO-CeO_2$ as they possess good UV-shielding ability (Yabe et al., 2001; Li et al., 2002; Tsuzuki et al., 2002; Yamashita et al., 2002; Sato et al., 2004; El-Toni et al., 2006b; Hayashi et al., 2009; Zhang and Lin, 2011; Zholobak et al., 2011).

In the Arctic area, ZrO_2 was added in the vehicle paints as it possesses good UV reflectance ability. For United State Army, in order to add UV protection to the soldier's uniform, nylon fibres were treated with ZrO_2 (Mark et al., 1991). As ZrO_2 has good UV-shielding ability, Hayashi et al. (2009) synthesized $ZnO-ZrO_2$ films with different concentration of ZrO_2 (0, 10, 20, 30 and 40 wt.%) using a single step sol-gel spin coating method. The resultant film with a $[Zn]/[Zr]$ of 70/30 exhibited lower transmittance in the UV region ($< 10\%$) compared to that of ZnO . This suggested that the incorporation of ZrO_2 in ZnO improves the UV-shielding ability compared to pure ZnO (Hayashi et al., 2009).

Although TiO_2 and ZnO have good UV-shielding ability but their high photocatalytic activity aids the generation of reactive oxygen species which have been paid much attention because of safety concerns (El-Toni et al., 2006a). Furthermore, the high refractive index of TiO_2 (anatase $n = 2.5$ and rutile $n = 2.72$) and ZnO ($n = 2.2$) compared to CeO_2 ($n = 2$) causes the skin to look unnaturally when these materials are used in cosmetic CeO_2 products (El-Toni et al., 2006b). By comparing with TiO_2 and ZnO , CeO_2 has better properties as it appears naturally on the skin, without imparting an excessively pale white look, and it has excellent UV absorption. However, CeO_2 has seldom been used commercially as sunscreen

materials as it has high catalytic activity for the oxidation of organic materials (Yabe et al., 2001). To overcome this problem, CeO₂ was doped with metal ions having larger ionic size and/or lower valence, such as Ca²⁺, Zn²⁺, Ba²⁺, Sr²⁺ and Mg²⁺ or incorporated with other oxides such as ZrO₂ and ZnO to reduce the oxidation catalytic activity and/or increase UV-shielding effect compared to pure CeO₂ (Yabe et al., 2001; El-Toni et al., 2006a; Hayashi et al., 2009; Zhang and Lin, 2011). As reported by Zhang and Lin (2011), Zr_{0.7}Ce_{0.3}O₂ which was prepared by a citric acid complexing route showed excellent UV absorption property compared to that of pure CeO₂.

Nowadays, natural raw materials are becoming scarce, whilst around the world, million tons of by-products after mineral processing are produced everyday and a disposal of these by-products is subject to ever stricter environmental legislation. However, some by-products are similar in composition to the natural raw materials used in industries and often contain materials that are also beneficial in the fabrication process. Thus, upgrading by-products to alternative raw materials is one of technological, economical and environmental interest (Menezes et al., 2009).

Tin slime, a by-product after a tin mining process, taken from an ex-mining field in Trong, Perak, Malaysia mainly contains kaolinite and minor amounts of gibbsite and muscovite. Clay minerals such as kaolinite, bentonite and mica have many benefits for human health and are already utilized in various types of pharmaceutical and cosmetic products. Thus, they are sought as the potential candidates in UV radiation protection (Carretero, 2002; Hoang-Minh et al., 2010). Hoang-Minh et al. (2010) have reported that clays such as kaolin, mica and bentonite

show potential for UV protection through the absorption and/or reflection of UV radiation.

Urea treatment is a well-known method to exfoliate the stacking layers of strongly aggregated particles, so-called a kaolin book (Ledoux and White, 1966; Pi et al., 2007; Valášková et al., 2007; Makó et al., 2009). Valášková et al. (2007) was successfully exfoliate kaolinite sample by an urea treatment method using a high-planetary ball milling (7700 rpm). However, in this study, the exfoliation of kaolinite sample was done by the urea treatment using a low-planetary ball milling (300 rpm).

As mentioned earlier, $Zr_{0.7}Ce_{0.3}O_2$ and kaolinite show the potential to be used as UV-shielding materials. However, reports on the preparation and the UV-shielding ability of the composite of these two materials are still not available yet. Thus, the goals of the present study were to prepare composite materials from $Zr_{0.7}Ce_{0.3}O_2$ and kaolinite/exfoliated kaolinite by three different synthesis methods including a citric acid complexing method, with and without NH_3 added, a soft solution chemical method, a hydrothermal treatment method, with and without sodium oleate added, and to compare the UV-shielding property of all the composite materials obtained thereof. The addition of NH_3 in the preparation of composite by citric acid complexing method was expected to improve the precipitation of $Zr_{0.7}Ce_{0.3}O_2$ on the particles of kaolinite/exfoliated kaolinite. In hydrothermal treatment method, sodium oleate was added to avoid the agglomeration of $Zr_{0.7}Ce_{0.3}O_2$ particles as reported by Taniguchi et al. (2009).

1.2 Research objectives

This study is focused on the preparation of kaolinite sample from tin slime, the exfoliation of kaolinite, the different synthesis methods of $Zr_{0.7}Ce_{0.3}O_2$ -kaolinite/exfoliated kaolinite composite and the UV-shielding property of the composite materials. Therefore, the objectives of this study are as follows:

- i. To purify tin slime which is a by-product after tin mining and mainly composed of kaolinite.
- ii. To exfoliate the stacking layers of kaolinite sample by an urea treatment method.
- iii. To apply different synthesis methods i.e. a solid mixing method, a citric acid complexing method (with and without NH_3) added, a soft solution chemical method and a hydrothermal treatment (with and without sodium oleate added) in order to produce $Zr_{0.7}Ce_{0.3}O_2$ -kaolinite/exfoliated kaolinite composite with a good dispersion of kaolinite/exfoliated kaolinite and $Zr_{0.7}Ce_{0.3}O_2$.
- iv. To compare the UV-absorbance property of the composite materials which were synthesized by different methods.

1.3 Project overview

All the essential elements in materials science and engineering are designed to be covered in this study as follows:

- a. Preparation of kaolinite from tin slime (which is a by-product of tin mining) by sedimentation or elutriation method.
- b. Preparation of exfoliated kaolinite from kaolinite by urea treatment method.
- c. Preparation of $Zr_{0.7}Ce_{0.3}O_2$, pure ZrO_2 and pure CeO_2 by different synthesis methods such as a citric acid complexing method (without NH_3 added), a soft

solution chemical method and a hydrothermal treatment (with and without sodium oleate added).

- d. Preparation of $Zr_{0.7}Ce_{0.3}O_2$ -kaolinite composites and $Zr_{0.7}Ce_{0.3}O_2$ -exfoliated kaolinite composites by a solid mixing method, a citric acid complexing method with and without NH_3 added, a soft solution chemical method and a hydrothermal treatment method with and without sodium oleate added.
- e. Comparison of the characterization results of urea treated kaolinite at different milling times (1, 3 and 5 h) to choose the best exfoliation of kaolinite and use it as exfoliated kaolinite in the preparation of composite materials.
- f. Comparison of the characterization results and UV-shielding property of $Zr_{0.7}Ce_{0.3}O_2$ -kaolinite composites and $Zr_{0.7}Ce_{0.3}O_2$ -exfoliated kaolinite composites which were prepared by different preparation methods and selection of the synthesis method which produced composite with the best UV-shielding property.
- g. Preparation and comparison of characterization results and UV-shielding property of composite materials which were prepared at different concentration of kaolinite or exfoliated kaolinite using the synthesis method that was used to prepared the best composite material as mention above.

CHAPTER 2

LITERATURE REVIEW

2.1 Solar radiation

Continuous thermonuclear reactions in the sun's core yield a wide spectrum of electromagnetic energy that radiates through space in all directions. The sun's radiant energy sustains all life on Earth. Solar energy not only maintains the Earth's temperature but also supports the growth of photosynthetic plants, which have the ability to convert radiant energy to chemical potential energy. Man obtains his own body fuel by ingesting both plant and plant-eating animals. Without sunlight, the surface of the Earth would be cold, still, and completely lifeless (Parrish et al., 1978).

Electromagnetic radiation from the sun contains a small proportion of ultraviolet (UV) radiation, about 7 % of the radiation striking the Earth's atmosphere and an even smaller proportion penetrating the atmosphere (Martyn, 1979). The sun is the main source of UV exposure for most people. The broad spectrum and intensity of the UV radiation emitted by the sun result from its very high surface temperature. The levels of UV radiation that reach the Earth's surface depend on the time of year, the transmission properties of the atmosphere, and the emission power of the sun (Dervault et al., 2005).

Sunlight undergoes absorption and diffraction in the outermost layers of the atmosphere, and then in the stratosphere and troposphere before reaching the Earth's surface. Absorption by the molecule oxygen (O₂) and absorption by ozone (O₃) are

the most important phenomena. The boundary between the troposphere and stratosphere is situated some 10 km from the Earth's surface. The stratosphere ozone layer, formed 10-40 km above the Earth's surface, in practice prevent all UV radiation with wavelengths under 290 nm and a substantial proportion (70-90 %) of radiation with wavelengths in between 280-315 nm from reaching the Earth's surface. The composition of the solar radiation spectrum at ground level is therefore between 290 and 400 nm.

At ground level, UV radiation consists of two major components: radiation received directly from the sun and radiation diffracted in the atmosphere. The ratio between direct and diffracted radiation varies with wavelength and height of the sun above the horizon. Individual exposure to solar UV radiation depends on geographical location, altitude, time of year, time of day, and possibly cloud cover. The spectral irradiance of UV radiation (at 300 nm) is at its peak at midday (local solar time) when the sun's elevation is at its height. This irradiance is at least ten times greater than the value observed before 9 a.m. (local solar time) or after 3 p.m. (local solar time). 70 per cent of exposure to UV radiation is therefore received during the four central hours of the day (local solar time), i.e. from midday to 4 p.m. in summer (Dervault et al., 2005).

2.2 Classification of electromagnetic spectrum and its effects on humans skin

It is convenient to give names to certain portions of the electromagnetic spectrum, but it is important to remember that the biologists' practical classifications of electromagnetic energy are, in part, an example of the arbitrary and egotistical nature of man. The names used by convention are related to a strange mixture of a

number of properties of the radiation, such as (1) wavelength, frequency or photon energy; (2) spectral relation to visible light or sunlight on Earth; (3) the apparent effects of the radiation on humans; and (4) the uses man has found for the radiation (Figure 2.1) (Parrish et al., 1978).

As described by Parrish et al. (1978), the electromagnetic spectrum has been divided as follows:

Visible light (wavelength of approximately 400-700 nm) is that radiation that passes through the human lens to be absorbed by specialized molecules in the retina and to stimulate central nervous system recognition of the event. Visible light also penetrates through skin and subcutaneous tissues, but under usual circumstances such photons do not cause photochemical events that are recognizable in the form of tissue alteration or damage. Of the familiar visible light color spectrum (Figure 2.1), the shortest wavelengths are perceived as violet, and the longest wavelengths are perceived as red. The invisible regions of the electromagnetic spectrum that neighbour the visible region are termed the *ultraviolet* and *infrared* regions. UV radiation consists of shorter-wavelength, higher-energy photons than violet light, and infrared radiation consists of longer-wavelength, lower-energy photons than red light.

The UV radiation region of the spectrum is subdivided into several bands in terms of phenomenological effects. Unlike these wavelength divisions, the effects of UV radiation do not terminate sharply at specific wavelengths. Furthermore, the subdivisions are arbitrary and differ somewhat, depending on the discipline involved. Photobiologists generally divide the UV spectrum into three portions, called UV-A,

UV-B, and UV-C, in order of decreasing wavelength (Figure 2.1 and 2.2). The wavelength range from 200 to 290 nm is called *UV-C*. Radiation of wavelength shorter than 200 nm is mostly absorbed by air, and solar radiation of wavelength below 290 nm does not reach the Earth's surface because of absorption by ozone formed in the stratosphere. The band from 290 to 320 nm is called *UV-B*, and the band from 320 to 400 nm is called *UV-A*. This terminology was originally derived by Coblenz in 1932, and is based on a combination of physical properties and biologic effects of each of these UV wavelength regions. The division between UV-C and UV-B is sometimes chosen as 280 nm, and 315 nm is sometimes chosen as the division between UV-B and UV-A. Since the divisions between UV-C, UV-B and UV-A are neither phenomenologically exact nor agreed upon, for critical work one should define UV radiation in more rigorous spectroradiometric terms.

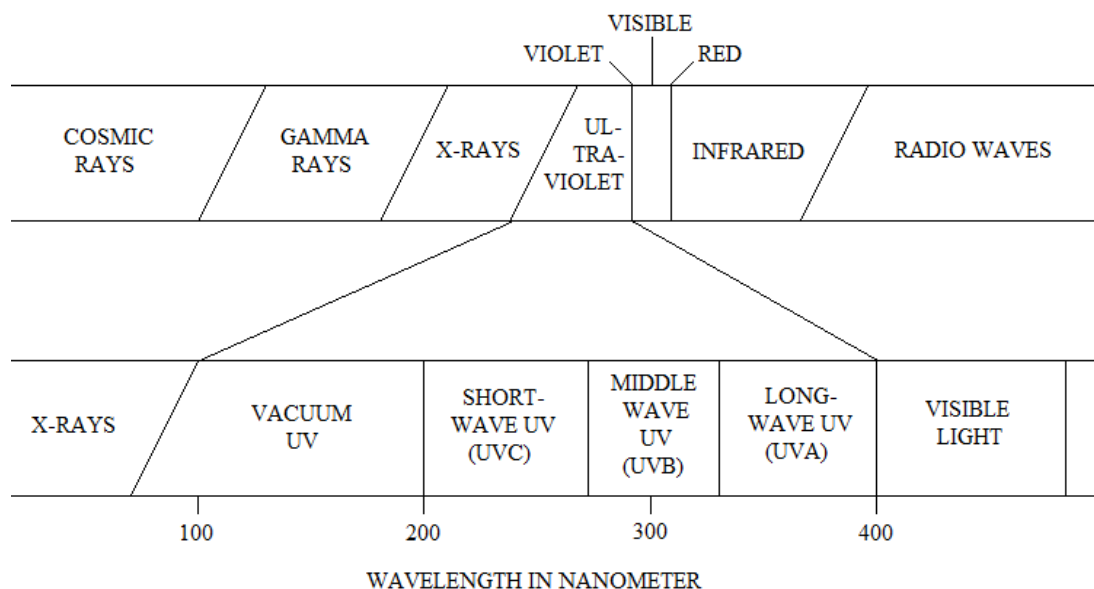


Figure 2.1: Electromagnetic spectrum with expanded scale of UV radiation (Parrish et al., 1978)

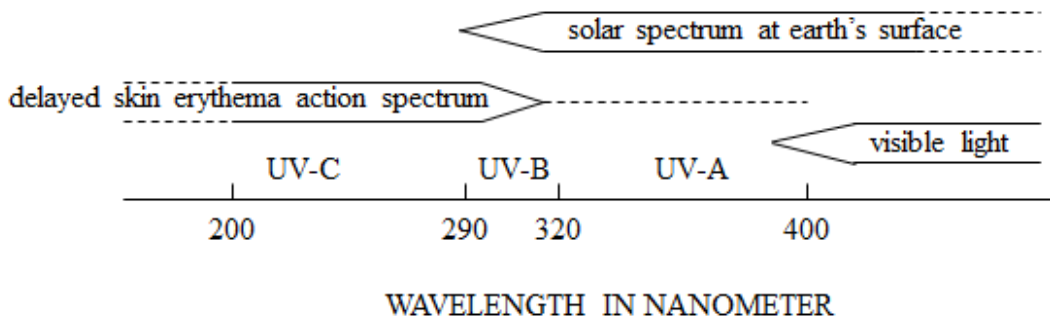


Figure 2.2: Graphic illustration of phenomenologic definition of UV-A, UV-B, and UV-C (Parrish et al., 1978)

UV-C is also called *germicidal radiation* because of its effectiveness in killing one-celled organisms. UV-C is often called *shortwave UV* because the wavelengths in this region are the shortest UV radiation transmitted through air. This UV region is the furthest from the visible spectrum and is also called *far UV*.

Solar UV radiation of wavelengths between 290 and 320 nm reaches Earth in relatively small quantities but is very efficient in causing sunburning of human skin. For this reason, it is often referred to as the *sunburn spectrum* or the *erythemal band*. Because of its relative spectral position, UV-B is also called *middle UV*, *mid UV*, or *middlewave UV*.

UV-A is sometimes referred to as *longwave UV* and *long UV* and is also called *near UV* because of its proximity to the visible spectrum. This spectral region has also been called the *blacklight region*, because its principal use for many years was to excite florescent and phosphorescent substances that reradiate the absorbed energy as light in the visible spectrum.

2.3 Advantages of sunlight on human health

Humans have evolved in sunlight and depend upon it for more than an indirect source of food. Our skin, blood vessels, and certain endocrine glands respond to radiation from various portions of the electromagnetic spectrum of the sun. Many of our daily rhythms are dependent upon the cycles of the sunlight. The sophisticated sensory mechanism of the eye transduces absorption of electromagnetic radiation into nerve impulses to provide an instantaneous detailed concept of the environment (Parrish et al., 1978).

The best-known benefit of sunlight is its ability to boost the body's vitamin D supply; most cases of vitamin D deficiency are due to lack of outdoor sun exposure. At least 1,000 different genes governing virtually every tissue in the body are now thought to be regulated by 1,25-dihydroxyvitamine D₃ (1,25[OH]D), the active form of the vitamin, including several involved in calcium metabolism and neuromuscular and immune system functioning (Mead, 2008; Reichrath and Nürnberg, 2008).

2.4 Disadvantages of sunlight on human health

Although sunlight has many benefits on human health but excessive amount on any life-supporting agent can be harmful. Sunlight can damage or kill living cells, including those of man, and gross changes may follow this microscopic damage. Sunlight causes sunburn, skin cancer, wrinkling and "aging" of the skin, inflammation of the eyes, and possibly cataracts. Physiologic and anatomic alterations and instinctual responses, customs, and lifestyle determine one's sun exposure. Thus, humans live in a complicated ecobalance with sunlight: it is essential to sustain life, yet excessive solar radiation may be harmful (Parrish et al., 1978).

The effects of radiation on an organism depend on the effects of the absorbed radiation on the cells of which the organism is composed. The cellular changes caused by exposure to electromagnetic energy are in turn caused by chemical reactions following the absorption of photons by molecules of the cell. Such photochemical reactions cannot take place unless radiation is absorbed. The effect on the cells depends on the presence of absorbing molecules within or around the cells. Absorption is a relatively precise phenomenon. Specific molecular structures absorb radiation of specific wavelength or quantum energy region. Therefore, the molecular structure of the biomolecules determines their absorption of radiation of various photon energies, or wavelengths (Parrish et al., 1978).

The penetration of UV radiation and light into human tissue is limited by scattering and absorption. The main absorbers of visible light in tissue are hemoglobin and its degradation products, melanins, flavins and carotenoids. Aromatic amino acids and nucleic acids are absorbers in the UV-B regions (Moan, 2004). Although visible light can penetrate through skin and subcutaneous tissues, it does not cause photochemical events that are recognizable in the form of tissue alteration or damage. However, UV radiation penetrates the skin and causes biological effects (Parrish et al., 1978).

Figure 2.3 indicates the penetration depths of UV and visible light into human skin. The main action of UV-B is believed to take place in the epidermis and in the basal cell layer, while UV-A has a dermal effect. About 5% of the radiation is reflected from the outer surface of the skin, *i.e.* from the dead layer called *stratum corneum*. The radiation coming back from the skin is composed of reflected radiation

and radiation scattered in the epidermis and dermis, and is called remitted radiation. Some of the absorption characteristics of melanin and hemoglobin/oxyhemoglobin contribute to the shape of the spectrum of the remitted radiation.

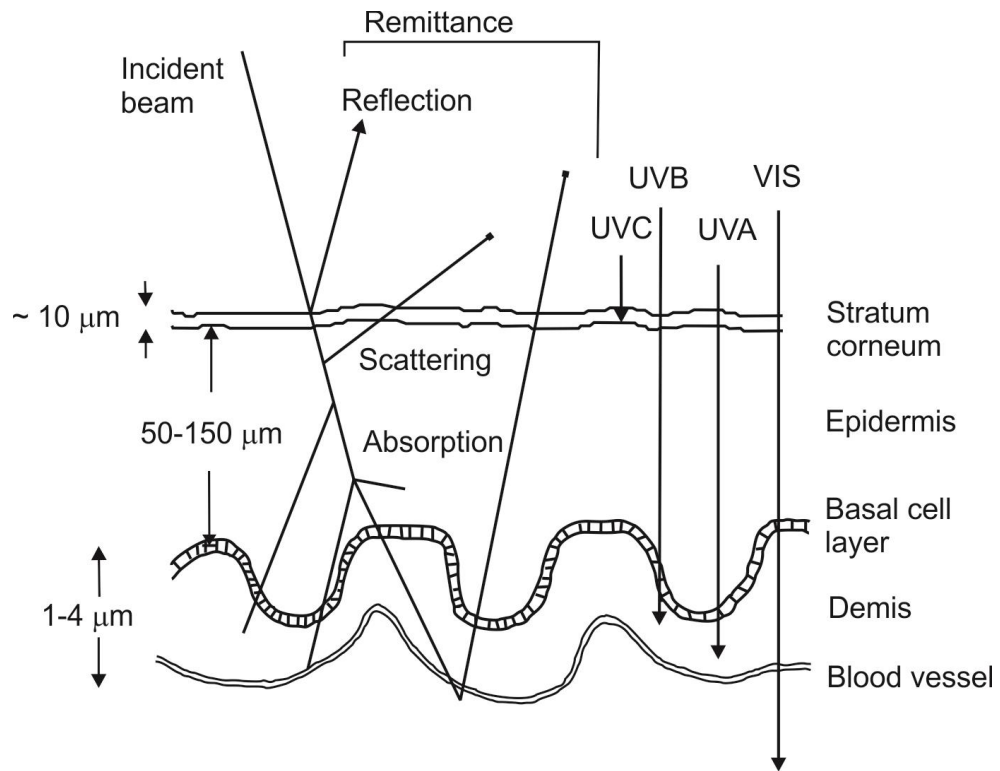


Figure 2.3: An illustration of absorption and scattering in skin (Moan, 2004).

Melanin plays a major role in the penetration of UV-B and UV-A through the epidermis. Thus, the transmittance at 300 nm is 2-3 orders of magnitude larger for white epidermis than for the darkly pigmented epidermis. Thickening (hyperplasia) of the epidermis is one of the reactions of human epidermis to UV. For UV-B, even mild hyperplasia plays a large protective role. However, for UV-A and visible light, hyperplasia offers little protection compared to melanogenesis. Melanin is present through the entire epidermis. Negoid *stratum corneum* contains melanin particles, melanosomes, while Caucasian; white *stratum corneum* contains only broken melanosomes, melano 'dust'. Urocanic acid is present in the epidermis of all people.

It has an absorption spectrum in the same spectral region as DNA and may play a protective role. Furthermore, it is believed that this substance is a main chromophore for UV effects on the immune system. Hemoglobin is present only in the vessels of the dermis but one of its break-down products, the lipophilic substance bilirubin, binds to fat and is present in the whole skin even in the stratum corneum. This is also true for ingested beta-carotene. These substances may act in two ways: partly as sunscreens and partly as antioxidants (Moan, 2004).

2.5 UV-shielding materials

Many researchers have paid much attention on the development of the UV-shielding materials since the level of UV radiation (UV) is being increased around the world (Mackie, 2000; Li et al., 2007). It is well-known that the UV radiation present in sunlight can lead to the development of melanoma, skin cancer, and perturbs the body's immune system (Li et al., 2007). Furthermore, it is detrimental to buildings, bleaching and fading the color of paintings, etc.

The damages caused by UV rays have been paid much attention and various kinds of UV-shielding materials have been designed in response. TiO_2 , ZnO and CeO_2 have been developed and they have been used as UV-shielding materials as they have good UV protection ability (Tsuzuki et al., 2002; El-Toni et al., 2006b; Zholobak et al., 2011). Besides the single oxides such as TiO_2 , ZnO and CeO_2 which possess good UV-shielding ability, mixed-oxide including $\text{ZrO}_2\text{-CeO}_2$, ZnO-ZrO_2 , $\text{CeO}_2\text{-CaO}$ and ZnO-CeO_2 also show good UV-shielding property compared to pure oxides alone (Yabe et al., 2001a; Li et al., 2002; Tsuzuki et al., 2002; Yamashita et al., 2002; Sato et al., 2004; El-Toni et al., 2006b; Hayashi et al., 2009; Zhang and

Lin, 2011; Zholobak et al., 2011). For example, Hayashi et al. (2009) developed ZnO-ZrO₂ films with different concentration of ZrO₂ (0-40 wt.%) using a single step sol-gel spin coating method. The resultant film with 70 wt.% of ZnO and 30 wt.% of ZrO₂ exhibited lower transmittance (<10 %) of UV radiation compared to that of pure ZnO. Another report by Zhang and Lin (2011) showed a significant improvement of UV-shielding ability of Zr_{0.7}Ce_{0.3}O₂ compared to pure ZrO₂ and CeO₂. This suggested that the incorporation of some oxides which have good UV-shielding property together can improve the UV-shielding ability of the final product compared to pure oxide alone.

There are also many reports on the development of UV-shielding materials from composite materials such as calcia-doped CeO₂/mica nanocomposite (El-Toni et al., 2006b), plate-like titanate/calcia-doped CeO₂ composite (Liu et al., 2009b), cerium oxide nanoparticles/epoxy composite thin film (Dao et al., 2011), etc. as they also have good UV-shielding ability.

2.6 Potential of ceramic composites as UV-shielding materials

2.6.1 Ceramics

Ceramics are defined as products made out of non-metallic and inorganic substances. On the other hand, ceramics is also defined as the art and science of making materials and products of non-metallic inorganic substances (Aldinger and Weberruss, 2010). Ceramics have been classified into three different types which are conventional ceramics, glasses and advanced ceramics as shown in Figure 2.4.

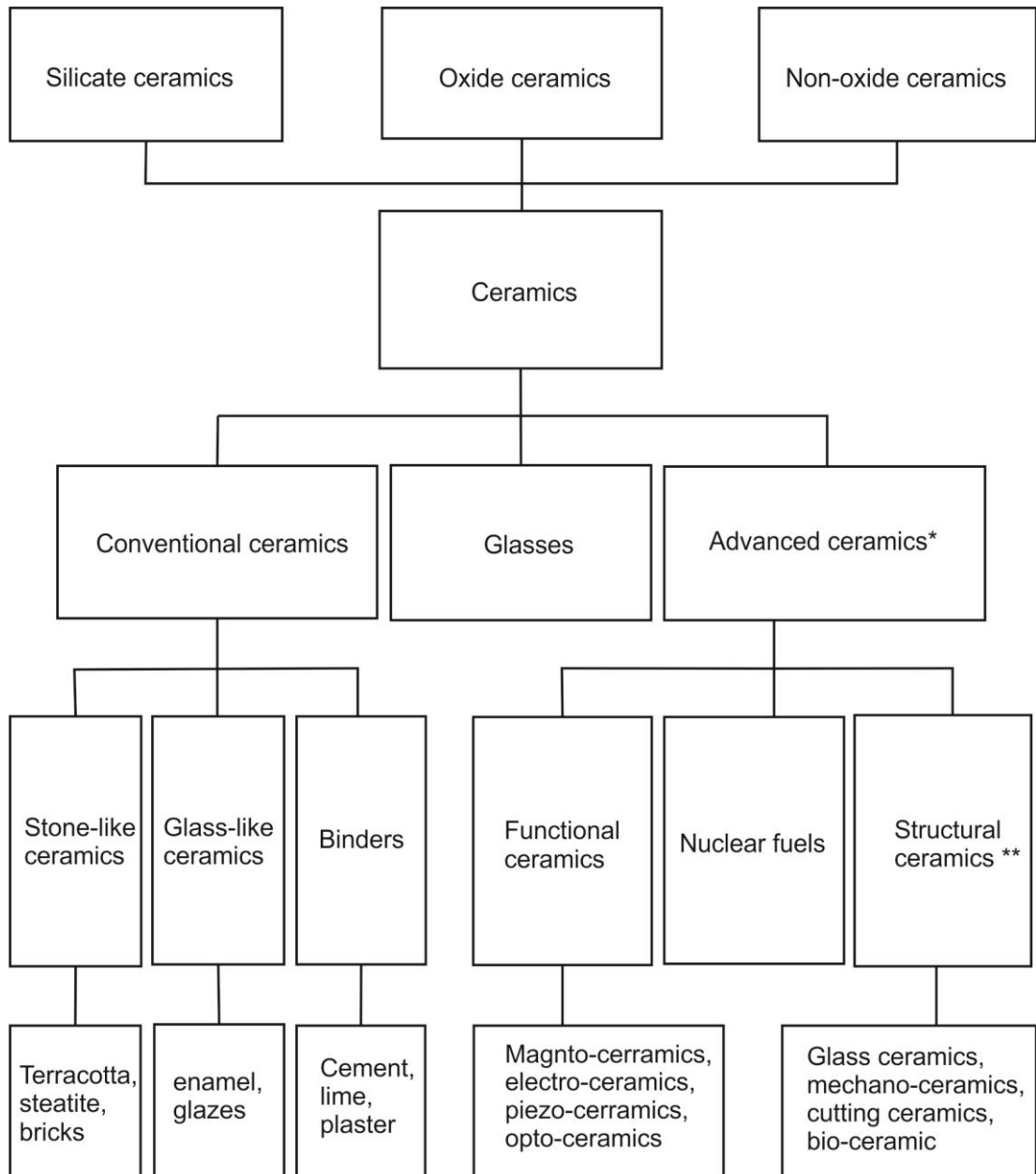


Figure 2.4: Classifications of ceramics (*frequently noted as “fine ceramics”, **frequently noted as “engineering ceramics”) (Aldinger and Weberruss, 2010).

2.6.1.1 Conventional ceramics

Conventional ceramics have been used by man since antiquity. The earliest conventional ceramic articles were made from naturally occurring materials such as clay minerals. It was discovered in prehistoric times that clay materials become malleable when water is added to them, and that a molded object can then be dried in

the sun and hardened in a high temperature fire (Net-Industries, 2012). Typically, conventional ceramics are the mixtures of many phases and made up of natural minerals like clay minerals (Bengisu, 2001).

2.6.1.1.1 Clay minerals

2.6.1.1.1.1 General Structure Features

Most common clay minerals are hydrous aluminum phyllosilicates, or layer silicates which are constructed from two molecular units: a sheet of corner-linked tetrahedra (Figure 2.5) and a sheet of edge-linked octahedra (Figure 2.6) (Bailey, 1980; Moore et al., 1997). Different clay mineral groups are characterized by the stacking arrangements of sheets of these units and the manner in which two successive two- or three-sheet layers are held together (Mitchell and Soga, 2005). This forms two basic layer types: ~0.7 nm thick 1:1 layer (i.e., consisting of 1 tetrahedral sheet and 1 octahedral sheet per layer) and ~1.0 nm thick 2:1 layer (i.e., consisting of 2 tetrahedral sheets and 1 octahedral sheet sandwiched between the tetrahedral sheets). The stacking of either 1:1 or 2:1 layers or a combination of both accounts for major structural differences among these minerals (as shown in Figure 2.7). The layers are held together by different interlayer complexes (e.g., hydrogen bond, non-hydrated cation, or hydrated cation), resulting in different interlayer bonding strength. The interlayer cations also compensate the net negative charges in the layers caused by isomorphous substitutions. Isomorphous substitution occurs when some of the tetrahedral and octahedral spaces are occupied by cations other than those in the ideal structure during initial formation and subsequent alteration of the clay minerals. It usually gives clay layers a permanent negative charge, thus creating the need for cations between the layers in order to preserve electrical

neutrality. These cations could be present either in fixed (e.g., K^+ in mica) or exchangeable positions (e.g., Na^+ , Ca^{2+} in smectite). Another type of charge occurs at the edges of mineral particles where structural patterns terminate with broken bonds. These unsatisfied bonds are usually satisfied by H^+ and OH^- which are dependent on the pH value of the environment. The variability of the permanent surface charge and pH dependent edge charge together with the various cations attracted dominates the complicated physicochemical properties of the clay minerals (Moore et al., 1997; Dixon et al., 2002; Mitchell and Soga, 2005).

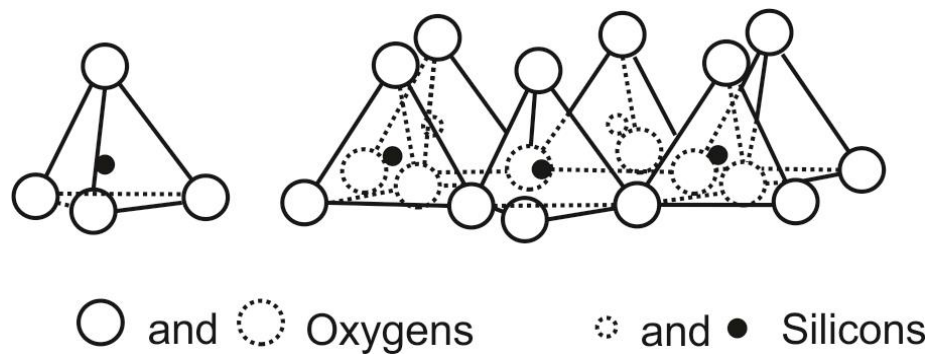


Figure 2.5: Silicon tetrahedron and corner-linked tetrahedral sheet (Goldman, 1990).

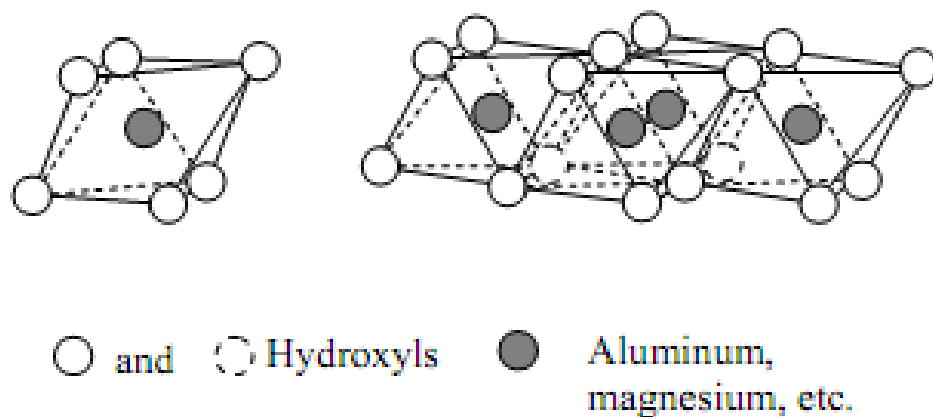


Figure 2.6: Octahedron unit and edge-linked octahedral sheet (Goldman, 1990).

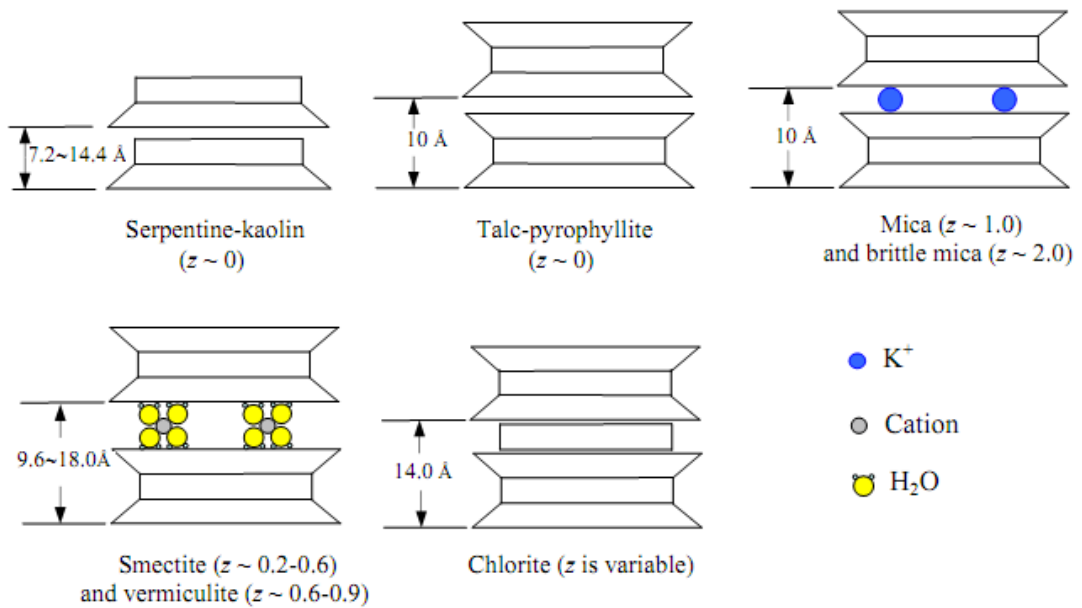


Figure 2.7: Schematic illustration of the crystal structures of major clay minerals. z is the negative charge per formula unit layer, $O_5(OH)_4$ for 1:1 layer minerals and $O_{10}(OH)_2$ for 2:1 layer minerals (Bailey, 1980; Brown and Nadeau, 1984; Moore et al., 1997; Mitchell and Soga, 2005)

2.6.1.1.2 Classifications

The clay minerals (Table 2.1) are classified in seven groups according to (a) the type of silicate layer present (1:1 or 2:1), (b) the magnitude of the net layer charge (ξ) per formula unit, and (c) the interlayer material that compensates the layer charge. Each group is divided into subgroups on the basis of the octahedral character (dioctahedral or trioctahedral with 2.5 cations as the boundary) (Martin et al., 1991).

Table 2.1: Classification of clay minerals (Martin et al., 1991)

| Interlayer material ^a | Group | Octahedral character ^b | Species |
|---|----------------------|-----------------------------------|---|
| <i>2:1 Clay minerals</i> | | | |
| None, $\xi \sim 0$ | Talc-pyrophyllite | Tri Di | Kerolite, pimelite, talc, willemsite Ferripyrophyllite, pyrophyllite |
| Hydrated exchangeable cations, $\xi \sim 0.2-0.6$ | Smectite | Tri | Hectorite, saponite, sauconite, stevensite, swinefordite |
| | | Di | Beidellite, montmorillonite, nontronite, volkonskoite |
| Hydrated exchangeable cations, $\xi \sim 0.6-0.9$ | Vermiculite | Tri | Trioctahedral cermiculite |
| | | Di | Dioctahedral vermiculite |
| Non-hydrated monovalent cations, $\xi \sim 0.6-1.0$ | True (flexible) mica | Tri | Biotite, lepidolite, phlogopite, etc. |
| | | Di | Celadonite, illite, glauconite, muscovite, paragonite, etc. |
| Non-hydrated divalent cations, $\xi \sim 1.8-2.0$ | Brittle mica | Tri | Anandite, bityite, clintonite, kinoshitalite |
| | | Di | Margarite |
| Hydrated sheet, ξ variable | Chlorite | Tri | Baileychlore, chamosite, clinochlore, nimite, pennantite |
| | | Di | Donbassite |
| | | Di-tri | Cookeite, sudoite |
| <i>Regularly interstratified 2:1 clay minerals</i> | | | |
| ξ variable | | Tri | Aliettite, corrensite, hydrobiotite, kulkeite |
| | | Di | Rectorite, tosudite |
| <i>1:1 Clay minerals</i> | | | |
| None or H ₂ O only, $\xi \sim 0$ | Serpentine-kaolin | Tri | Amesite, berthierine, brindleyite, cronstedtite, fraipontite, kellyite, lizardite, nepouite |
| | | Di | Dickite, halloysite (planar), kaolinite, nacrite |
| | | Di-tri | Odinite |

^a ξ = net layer charge per formula unit.

^b tri = trioctahedral, di = dioctahedral.

2.6.1.1.1.2.1 The 2:1 layer

The layer of 2:1 phyllosilicates consists of an octahedral sheet sandwiched between two opposing tetrahedral sheets as shown in Figure 2.8. In pyrophyllite (dioctahedral) and talc (trioctahedral), the layer is electrically neutral. In the other 2:1 phyllosilicates (e.g., smectite, vermiculite, mica, chlorite), the layer is usually negatively charged (Brigatti et al., 2006).

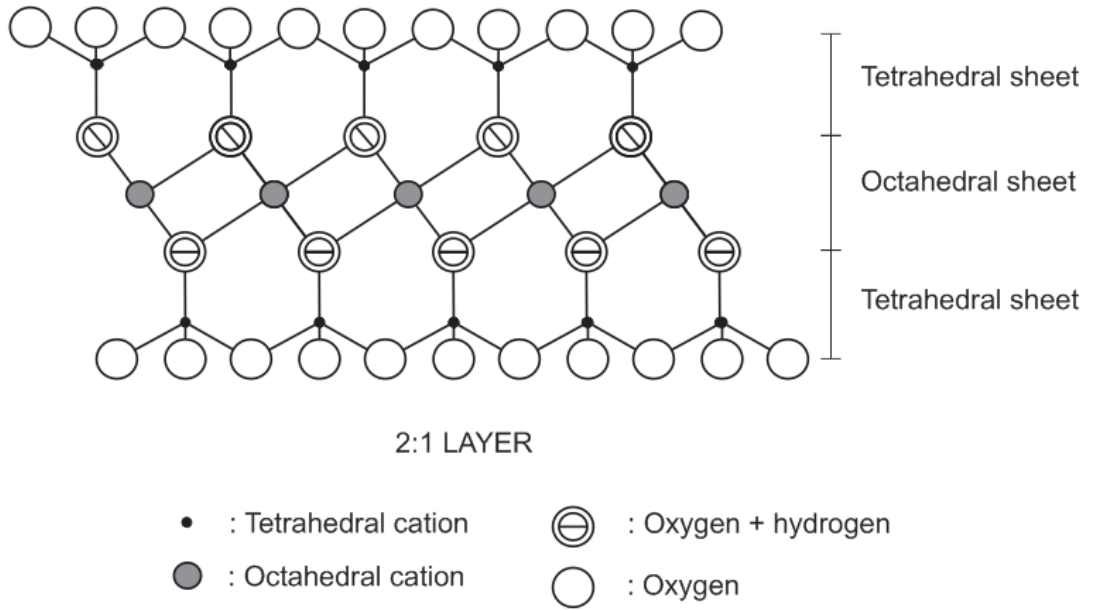


Figure 2.8: Junction of sheets to form 2:1 layer (Brindley and Brown, 1980)

2.6.1.1.2.2 The 1:1 layer

The 1:1 clay mineral type consists of one tetrahedral sheet and one octahedral sheet (Figure 2.9). These two sheets are approximately 7 Å thick. This two-sheet type is divided into kaolinite (dioctahedral) and serpentine (trioctahedral) group (Weaver and Pollard, 1973).

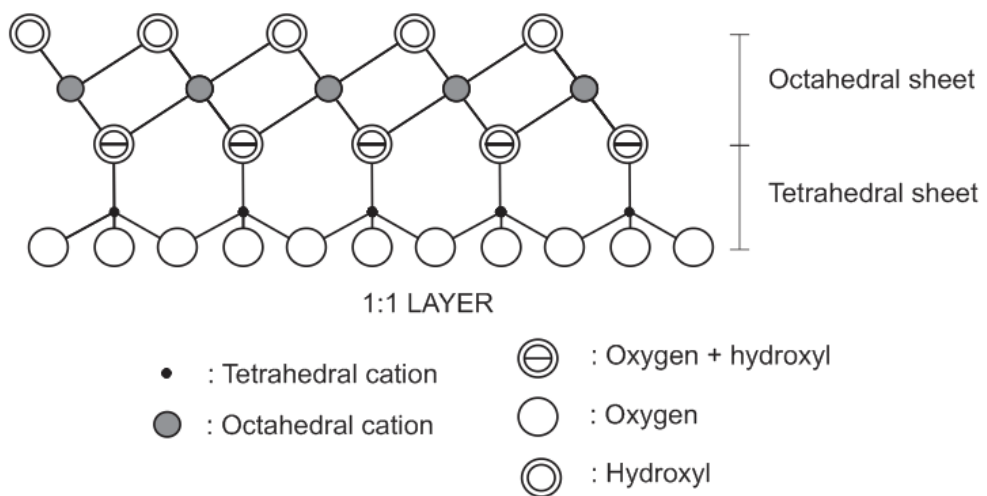


Figure 2.9: Junction of sheets to form 1:1 layer (Brindley and Brown, 1980)

A. Trioctahedral 1:1 minerals: The serpentine group

Lizardite, antigorite, and chrysotile are Mg-rich 1:1 trioctahedral layer minerals with an ideal composition of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. Although chemically simple, they are structurally complex. Lizardite has an ideal layer topology, whereas antigorite is modulated and chrysotile is bent (Wicks and Whittaker, 1975; Wicks and O'hanley, 1988; Veblen and Wylie, 1993).

These structural differences are recognized by the AIPEA Nomenclature Committee (Martin et al., 1991). Like lizardite, the trioctahedral 1:1 minerals berthierine, amesite, cronstedtite, nepouite, kellyite, fraipontite, and brindleyite have been classified as serpentine minerals with a planar structure. Other minerals, traditionally referred to as serpentine, show a modulated layer structure. They are subdivided into minerals with tetrahedral sheet strips such as antigorite and bementite, or with tetrahedral sheet islands such as greenalite, caryopilite, pyrosmalite, manganpyrosmalite, ferropyrosmalite, friedelite, mcgillite, schallerite, and nelenite (Brigatti et al., 2006).

B. Dioctahedral 1:1 Minerals: The Kaolin Group

The clay minerals in the kaolin group consist of dioctahedral 1:1 layer structures with a general composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Kaolinite, dickite, and nacrite are polytypes. The kaolinite stacking sequence consists of identical layers with an interlayer shift of $2a/3$ (Brigatti et al., 2006). Dickite and nacrite have a two-layer stacking sequence where the vacant site of the octahedral sheet alternates between two distinct sites (Brindley and Brown, 1980). Halloysite is a hydrated polymorph of kaolinite with curved layers and a basal spacing of 1 nm that decreases

to about 0.7 nm on dehydration. The composition of the kaolin group minerals is characterized by a predominance of Al^{3+} in octahedral sites, although some isomorphous substitution of Mg^{2+} , Fe^{3+} , Ti^{4+} , and V^{3+} for Al^{3+} can occur (Brigatti et al., 2006).

a. Kaolinite

Kaolinite is by far the most abundant species of the kaolinite subgroup. Although hundreds of chemical analyses of this clay have been made, there is still little known for certain about the exact composition of most samples. The ideal composition for the kaolinites $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$ is: 46.54% SiO_2 , 39.5% Al_2O_3 , 13.96% H_2O ; however, in nature, this exact composition is seldom, if ever, found because of the presence of accessory minerals (Weaver and Pollard, 1973).

Fe_2O_3 , TiO_2 , MgO , and CaO are nearly always present in kaolinite samples and K_2O and Na_2O are usually present. Most samples either have excess SiO_2 or Al_2O_3 . Mineral impurities such as quartz, anatase, rutile, pyrite, limonite, feldspar, mica, montmorillonite and various iron and TiO_2 are commonly present in addition to a number of other minerals. Si and Al, in the form of hydroxides, apparently can occur as coatings on the kaolinite layers. Although many of these impurities are usually identified, seldom is the analysis sufficiently quantitative to determine if all the deviation from the ideal composition is due to these impurities (Weaver and Pollard, 1973).

Kaolinite is mined and processed in a number of countries and it serves as an important industrial mineral used in the manufacture of ceramics, medicine, coated