STRUCTURAL AND LUMINESCENCE PROPERTIES OF MAGNESIUM SILICO-PHOSPHATE DOPED WITH EUROPIUM AND DYSPROSIUM IONS

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This thesis is dedicated to my

beloved husband, parents and family.

Thank you for being with me all along.

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ABSTRACT

Phosphor materials based on magnesium silico-phosphate was prepared via solid-state reaction method. The series of samples were in the form of xMgO (70-x) $SiO_2 30P_2O_5$: yEu_2O_3, zDy_2O_3 with $0 \leq x \leq 30$ mol %, $0 \leq y \leq 1$ mol % and $0 \leq z \leq 4$ mol %. The X-ray diffraction pattern confirms that the synthesized material consists of SiO_2, SiP_2O_7, $Mg_2P_4O_{12}$ and $MgSiO_3$. FTIR spectroscopy was carried out to investigate the structure feature and vibrational study of phosphor material. The introduction of MgO yields the oxygen bridge like SiO^-, PO^-, Si-O-Si, P-O-P and Si-O-P linkages and was revealed that the hydroscopic properties from P_2O_5 can be reduced. Other than that MgO also take part in the formation of P=O:Mg by the breakdown of the vibration of double bond, P=O. The morphology and grain size of phosphor material was studied using SEM. It proves that doping material addition changes the morphology of host system. EDAX study was employed to give a clear evidence of doping material that had been used in this study. The photoluminescence characteristics originating of europium and dysprosium trivalent were also investigated. The addition of Dy^{3+} as co-dopant in the 20MgO-50SiO_2-30P_2O_5: 1Eu_2O_3 shows the quenching effect in the emission spectra. The photoluminescence intensity of Eu^{3+} decrease gradually with the concentration of the co-dopant in the range from 1 mol% to 4 mol%. The significantly intense emission peak was obtained at 474 nm (blue), 563 nm (yellow), 585 nm (orange), and 610, 645, and 658 nm (red) for 20MgO-50SiO_2-30P_2O_5: 1Eu_2O_3, 1Dy_2O_3. The energy absorbed by Dy^{3+} is transferred to Eu^{3+} and energy levels at each transition were provided. The transition of Eu^{3+}, $^5D_0 \rightarrow {}^7F_2$ and Dy^{3+}, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ are hypersensitive electronic dipole transition and greatly affected by the coordination environment which are located at low-symmetry local site. Experimental results revealed that the luminescence can be affected by crystal structure, doping material concentration and morphology.

ABSTRAK

Bahan fosfor berasaskan kepada siliko-fosfat telah disediakan melalui kaedah tindakbalas keadaan pepejal. Siri sampel dalam bentuk xMgO (70-x) $SiO_2 30P_2O_5$: yEu_2O_3, zDy_2O_3 dengan $0 \leq$ x mol % ≤ 30 mol $0 \leq$ y mol≤ 1 dan $0 \leq$ z mol%≤ 4 telah disediakan. Corak pembelauan sinar-X (XRD) menunjukkan bahawa sintesis terdiri daripada SiO_2, SiP_2O_7 $Mg_2P_4O_{12}$ dan $MgSiO_3$. Spektroskopi FTIR dilakukan untuk menyiasat ciri-ciri struktur dan mengkaji getaran bahan fosfor. Pengenalan MgO menyebabkan berlakunya jambatan oksigen seperti SiO^-, PO^-, Si-O-Si, P-O-P dan hubugan Si-O-P yang membongkarkan sifat hidroskopik dari P_2O_5 dapat dikurangkan. MgO juga mengambil bahagian dalam pembentukan P=O:Mg dengan memusnahkankan getaran ikatan ganda dua, P=O. Morfologi dan saiz butiran bahan fosfor ditunjukkan oleh SEM. Ia membuktikan bahawa penambahan bahan dop telah mengubah morfologi sistem perumah. Kajian berdasarkan EDAX telah digunakan untuk menerangkan dengan jelas mengenai bahan dop yang telah digunakan dalam kajian ini. Ciri-ciri pendarcahaya berasal dari trivalensi Europium dan Dysprosium juga dikaji. Penambahan ion Dy^{3+} sebagai co-dopan di dalam $20MgO\text{-}50SiO_2\text{-}30P_2O_5$: $1Eu_2O_3$ menunjukkan kesan pemadaman di dalam spektrum pancaran. Keamatan pendarcahaya Eu^{3+} dari penurunan secara beransur dengan pertambahan co-dopan dalam julat dari 1 mol% hingga 4 mol%. Keamatan puncak pancaran yang penting telah diperolehi di 474 nm (biru), 563 nm (kuning), 585 nm (oren), dan 610, 645, dan 658 nm (merah) untuk $20MgO\text{-}50SiO_2\text{-}30P_2O_5$: $1Eu_2O_3$, $1Dy_2O_3$. Tenaga yang diserap oleh Dy^{3+} telah dipindahkan kepada Eu^{3+} dan aras tenaga pada setiap peralihan disediakan. Peralihan Eu^{3+}, $^5D_0 \rightarrow {}^7F_2$ dan Dy^{3+}, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ peralihan dwikutub sensitif elektronik sangat dipengaruhi oleh keadaan persekitaran di bahagian tempatan simetri-rendah. Keputusan kajian menunjukkan bahawa pendarcahaya boleh dipengaruhi oleh struktur kristal, konsentrasi bahan dop dan morfologi.

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LIST OF SYMBOLS AND ABREVIATIONS

ZnS	Zinc Sulphide
MgO	Magnesium Oxide
SiO_2	Silicon Oxide
P_2O_5	Phosphate
UV	Ultraviolet
Eu^{3+}	Europium (III) ions
Dy^{3+}	Dysprosium (III) ions
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
ICDD	International Centre for Diffraction Data
EDAX	Energy Dispersive X-ray Analysis
FTIR	Fourier Transform Infrared
LED	Light Emitting Diode
E	Energy
F	Force (energy)
λ	Wavelength
d	spacing between the planes
D	average dimension of crystallites
H	Plank’s constant
Y	Frequency
δ	Bending

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Luminescent materials are not new, they have been observed in nature such as in algae, some of bacteria, firefly and jellyfish. These materials are interesting due to their ability to glow by themselves with attractive colour. Their properties give inspiration to many researchers to develop new luminescent material with better durability and stability.

From century, researches of luminescent material made discovery at many research institutions. This research field has opened up unexpected applications such as in security, decoration, toys, lasers, semiconductor, transportation and also medication. Some of the products such as fluorescent lamp, television monitor, warning signs, escape routes, luminous paints, laser detection, light emitting diodes and toys and so on. All these application materials were called luminescent materials or phosphor materials whereas in inorganic solids, materials which depend on impurities and defect in the structure (Blasse,1994). The impurities and defect in the structure is referred to doping material.

In most cases, efficient phosphors comprise highly purified and well-crystallized bulk material, which is called host material and containing a small per cent of impurities, which is called activators (Leverenze, 1968). Luminescence host need to be stable crystal structure, high physical and chemical stability and high quantum efficiency especially for lamp phosphor (Barry, 1968: Bo Liu *et al.*, 2005: Yamazaki, 1986).

Until now, the most efficient long-lasting phosphors are still based on alkaline-earth aluminates and sulphide, for example $SrAl_2O_4$:Eu^{2+},Dy^{3+} produced green colour, $CaAl_2O_4$:Eu^{2+},Nd^{3+} produced deep blue colour and Y_2O_2S:Eu^{3+},Ti^{4+},Mg^{2+} produced red colour (Matsuzawa, 1986). Aluminates based phosphors have been replacing sulphide base. This is due to the aluminates had provide interesting and useful result such as no radiation, high brightness and long afterglow. But the properties of these phosphors may be decreased greatly when soaked in water for several hours (Aitasalo, 2005). Nowadays, alkaline earth silicate are regarded as suitable host with stable crystal structure, water-resistant property, high physical and chemical stability compared to sulphide phosphorescent phosphors and strontium aluminates phosphor (Yamazaki, 1986). It is also easy in preparation and low cost. Therefore, silicate host was attracting more attention in the application of long afterglow phosphor (Bo Liu *et al.*, 2005) and considerable attention had been paid because of its multi-colour phosphorescence and resistance to acid, alkali and oxygen.

However, in order to prepare silicate host material, high temperature is needed for phase formation in range 1200°C to 1400°C. For example long afterglow $Ca_2MgSi_2O_7$:Eu, Dy, $Sr_2MgSi_2O_7$:Eu, Dy and $Ba_2MgSi_2O_7$:Eu, Dy phosphors were prepared via sintering at 1300°C for 3 hours (Yuanhua Lin *et al.*, 2003). Silicate host needs some chemical that can cooperate with it to reduce the temperature of sample preparation. As an alternative, addition of phosphate into silicate is suggested to overcome this problem due to its low melting point and able to reduce temperature of phase formation. In other hand, phosphate presents a considerable interest with the low-softening temperature, ultra-violet transmission and high thermal coefficients (Ehrt and Seeber, 1991). In order to reduce the preparation temperature, William, 2006 reported about firing temperatures range for forming of crystal silicates from 1000 to 1300°C and 900 to 1200°C for phosphate. When mixed both of silicate and phosphate, the melting points of the mixtures might be lower than those the single compound. For example, the melting points curve of the system Zn_2SiO_4:Be_2SiO_4 decreases from 1510°C to a eutectic point of about 1170°C (William, 2006). Thus, combining the low melting point of phosphate with high water durability of silicate represents a tremendous potential for desired host materials. Furthermore, silicate is cheaper and abundant compared to other host materials.

Nevertheless, the poor chemical durability, high hydroscopic and volatile nature of phosphate (Rada and Culea, 2009) will decrease the degree of physical properties of silicate-phosphate base. In order that, alkali earth; MgO will be used as modifier on improving the physical properties in silicate-phosphate base. MgO crystal is transparent and good transmission of light ultraviolet to infrared ranges and electrical and thermal resistivity are also excellent.

As known, efficient luminescence performance can be improved greatly when they are doped with suitable auxiliary activator. Activator means doping material represented by either rare earth ions, transition metal ions or some ions which are capable to achieve the desired luminescent properties such as high brightness intensity and long afterglow. It can produce emission wavenumber from ultraviolet, visible light to infrared. The emission in visible light is interesting in the luminescent study because this range is suitable in various applications like mercury vapour lamp, bar code scanning laser and also LED. Every doping ion has their emission characteristic and it also depends on host materials. For examples: Zn_2SiO_4:Mn^{2+} emission at 525 nm (green), $Ca_2P_2O_7$:Dy^{3+} emission at 480 and 575 nm (white) (Leverenze, 1986) and $Ca_3MgSi_2O_8$:Ce^{3+} emission at 384 nm (blue) (Huang Lihui, 2000). As a consequence, doping materials are very important to determine the emission. Several host silicate doped with rare earth (R^{n+}) ions, either divalent or trivalent, have been proposed for or used as commercial phosphors in tricolour fluorescent lamps, scintilators and so on (Leverenze, 1968). For example, long afterglow phosphor based on alkaline earth silicate containing Eu^{2+}, Dy^{3+}, and Nd^{3+} ions was studied by Bo Liu *et al.*, (2005) and Ling Jiang *et al.*, (2004). Eu^{3+} and Dy^{3+} ions widely used of red and potential white phosphor were reported (Xiuzhen Xiao and Bing Yan, 2006). The interesting of both ions as doping material in phosphor is that they are hypersensitive, which are influenced strongly by the local structure (Qiang Su *et al.*, 1995).

From earlier studies by previous author, Poort, many works on luminescent materials used the conventional method which solid state reaction for preparing sample (Poort *et al.*, 1996). This method is easy and suitable for preparing powder sample with average particle size in range 10-20 µm (Yun Chan Kang *et al.*, 1999). No detailed study relating the effect of crystallinity, local structure and morphology to the luminescent properties of the alkali earth silicophosphate role as host materials has been performed to date. Therefore, this study will highlight relating the phase crystallinity, molecular vibration and morphology to the luminescence properties of the phosphor powder samples.

1.2 Problem Statement

A considerable amount of work has been reported on the luminescence properties of phosphor host material likes silicate, sulphide, aluminates and borate. They are excellent in luminescent properties such as stable crystal structure, long afterglow and high brightness, although, there have been several reports that those phosphor host material need high preparation temperature in range above 1300 °C. In order to reduce the high preparation temperature, another chemical such as phosphate need to be added into the host. Thus, this study will investigate structural and luminescence properties of magnesium silicophophate system doped with Eu^{3+} and Dy^{3+} ions phosphors. It is a new host material in order to get good properties of host material such as good crystal structure, water-resistant property, chemical stability, increase the strength, reduce the temperature of preparation and hydroscopic. Thus, this study will present the structure features of the samples and useful for future researchers in order to understand more about new host phosphor material properties. This study will also provide luminescence spectra of this system which is prepared by solid state reaction method and signify the relationship of the crystal structure, morphology and grain size with luminescence properties of the samples.

1.3 Objective of the Study

The objectives of this study are:

1. To determine the crystalline phase of the doped and undoped magnesium silicophosphate.
2. To determine the structure feature of magnesium silicophosphate and influence of modifier (magnesium) in the silicophosphate system.
3. To determine luminescent properties of the silicophosphate by doping with Eu^{3+} and Dy^{3+}.
4. To determine the correlation between the influence of doping Eu^{3+}, Dy^{3+} and concentration of Dy^{3+} on morphology, grain size and luminescent properties of the phosphor samples.

1.4 Scope of the Study

Magnesium silicophosphate

The samples of phosphor based host material on composition of magnesium silicate-phosphate doped with europium and dysprosium ions will be studied using MgO, SiO_2 and P_2O_5.

Phase and crystallinity of the synthesized compositions will be investigated by powder X-ray Diffraction (XRD). The structure feature of the samples will be measured using Fourier Transform Infra-red (FTIR) spectroscopy. The SEM and EDAX device will be used to investigate the grain size and surface morphology. The emission spectra will be carried out from photoluminescence (PL) instrument.

1.5 Significant of the Study

From early study in the luminescent field, researchers made a lot of findings of phosphor materials and their applications in industries even in the daily life. This research wants to develop phosphor based material on silicophosphate because of it has the potential in the structure and luminescence properties.

This study will create new phosphor materials which are cheap, easy to prepare, high brightness, no radiation and various applications. It also will come out with great luminescent properties of new phosphor materials.

From this study, it is promising to contribute new knowledge in the luminescent industry and for future study.

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