

**STRUCTURAL AND LUMINESCENCE PROPERTIES OF MAGNESIUM
STRONTIUM METAPHOSPHATE DOPED WITH EUROPIUM AND
DYSPROSIUM IONS**

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DYSPROSIUM IONS

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To my *Abah* and *Mama* who have given me much more
than these few words can say.

For my siblings and fiancé, thanks for the
patience, love and prayers.

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ABSTRACT

A series of samples based on $x\text{MgO}-(50-x)\text{SrO}-50\text{P}_2\text{O}_5$ (with $0 < x < 50$ mol %) were prepared using solid state reaction method and sintered at 900°C . The crystalline phase of powder samples were characterized using X-ray diffraction (XRD) while the assignments of the vibration modes were determined using Fourier Transform Infrared (IR) and Raman spectroscopies. The XRD analysis indicated that the prepared samples were polycrystalline phase of $\text{Sr}(\text{PO}_3)_2$, SrMgP_2O_7 , $\text{Mg}_2\text{P}_4\text{O}_{12}$ and $\text{Mg}_2\text{P}_2\text{O}_7$. The optimum sintering temperature of the prepared samples is 900°C . The Infrared and Raman studies showed that the magnesium strontium metaphosphate system consists of a main network of Q^2 , Q^1 and Q^0 tetrahedral units. There were four peaks observed in the both spectra which are P=O group (1320 cm^{-1}), PO_2 group ($1200 - 1170\text{ cm}^{-1}$), PO_3 and PO_4 groups ($1160 - 950\text{ cm}^{-1}$) and P-O-P group ($950 - 704\text{ cm}^{-1}$). This study illustrated that SrO and MgO act as modifiers and also improved chemical and physical stability of the phosphate material. The dopant ions (Eu^{3+} and Dy^{3+}) as studied using XRD, IR and Raman spectra showed that small quantities of europium and dysprosium ions does not affect the local structure of magnesium strontium metaphosphate network. The luminescence property of the Eu^{3+} and Dy^{3+} as dopants in magnesium strontium metaphosphate was studied using photoluminescence spectroscopy. The emission peaks for Eu^{3+} doped sample were located at 568 nm, 582 nm, 605 nm, 642 nm and 689 nm, due to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transition. Meanwhile for Dy^{3+} doped sample, two intense peaks appear at 477 nm and 564 nm are due to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transitions. For sample doped with Eu^{3+} and Dy^{3+} , the intensity of the main peak increases. This study also showed that magnesium strontium metaphosphate doped with Eu^{3+} and Dy^{3+} has better luminescence characteristic as compared to strontium metaphosphate or magnesium metaphosphate. The results of the study suggested that magnesium strontium metaphosphate is a potential candidate for plasma display applications.

ABSTRAK

Satu siri sampel berasaskan sistem $x\text{MgO}-(50-x)\text{SrO}-50\text{P}_2\text{O}_5$ (dengan $0 < x < 50$ mol %) disediakan melalui kaedah tindak balas keadaan pepejal dan disinter pada suhu 900°C . Kehabluran bagi sampel-sampel diciri menggunakan pembelauan sinar-X (XRD) manakala sifat-sifat getaran ditentukan dengan menggunakan serapan infra merah (IR) dan spektroskopi Raman. Analisis XRD menunjukkan sampel-sampel berada pada fasa polihabluran $\text{Sr}(\text{PO}_3)_2$, SrMgP_2O_7 , $\text{Mg}_2\text{P}_4\text{O}_{12}$ dan $\text{Mg}_2\text{P}_2\text{O}_7$. Suhu optimum pensinteran sampel ialah 900°C . Kajian serapan infra merah dan Raman menunjukkan sistem magnesium strontium metafosfat mengandungi rangkaian utama Q^2 , Q^1 dan Q^0 fosfat tetrahedron. Terdapat empat puncak pada kedua-dua spektrum iaitu kumpulan $\text{P}=\text{O}$ (1320 cm^{-1}), kumpulan PO_2 ($1200 - 1170\text{ cm}^{-1}$), kumpulan PO_3 dan PO_4 ($1160 - 950\text{ cm}^{-1}$) dan kumpulan P-O-P ($950 - 704\text{ cm}^{-1}$). Kajian menjelaskan penambahan SrO dan MgO bertindak memantapkan kestabilan kimia dan fizikal bahan fosfat. Bahan pendop (Eu^{3+} and Dy^{3+}) yang dikaji menggunakan spectrum XRD, infra merah dan Raman menunjukkan kuantiti kecil ion europium dan disprosium tidak menjejaskan rangkaian struktur magnesium strontium metafosfat. Pencirian luminesen Eu^{3+} dan Dy^{3+} sebagai bahan pendop dalam magnesium strontium metafosfat diukur menggunakan spektroskopi fotoluminesen. Puncak pemancaran bagi sampel didop dengan Eu^{3+} ialah pada 568 nm, 582 nm, 605 nm, 642 nm dan 689 nm, disebabkan peralihan $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j= 0, 1, 2, 3, 4$). Sementara itu untuk sampel didop Dy^{3+} , dua puncak pancaran utama dilihat pada 477 nm dan 564 nm yang disebabkan oleh peralihan pada $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ dan $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$. Untuk sampel yang didop dengan kedua – dua ion iaitu Eu^{3+} dan Dy^{3+} , keamatan puncak utama semakin meningkat. Kajian juga menunjukkan magnesium strontium metafosfat yang didop dengan Eu^{3+} and Dy^{3+} mempunyai puncak pancaran yang lebih tinggi berbanding dengan strontium metafosfat atau magnesium metafosfat. Keputusan kajian mencadangkan magnesium strontium metafosfat sebagai salah satu calon yang berpotensi untuk aplikasi paparan plasma.

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LIST OF SYMBOLS

δ	-	Deformation
ν_{as}	-	Asymmetric Stretching
ν_s	-	Symmetric Stretching
E	-	Energy
λ	-	Wavelength
S	-	Spin angular momentum
L	-	Orbital angular momentum
J	-	Total angular momentum
l	-	Azimuthal quantum number
c	-	Speed of Light
ν	-	Frequency of light
d	-	Distance
θ	-	Angle
h	-	Planck constant
Q	-	Tetrahedral of phosphate link

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Luminescence is related to the basic science as well as to the applied science. The word luminescence was first used by Eilhardt Wiedemann, a German physicist, in 1888 which means light (Williams, 1966). Nowadays, luminescence is observed with all phases of matter including gases, liquids and solids both organic and inorganic. The commercial importance of luminescence is ubiquitous, being manifest in displays, lamps, biochemistry, environmental sciences, pharmaceuticals and others fields. In nature, luminescence exists in fireflies, insects, fishes, mushrooms and luminescent bacteria.

Luminescence can be defined as the generation of light in excess of thermal radiation. Excitation of the luminescence substance is prerequisite to luminescent emission. There are several types of luminescence depending on their source of

excitation which are photoluminescence, cathodoluminescence, electroluminescence, triboluminescence and chemiluminescence.

Materials that can generate luminescence are called phosphors. Commercial phosphors are mostly inorganic compounds prepared as powders, glasses or thin films (Cees and Alok, 2006). Phosphor materials have attracted much attention because of their application to flat panel displays (FPD), including field-emission displays (FED). The long after glow phosphor is a special property in luminescence field of research. It can maintain the phosphorescence for several hours at room temperature. In the early time, zinc sulphide doped cobalt and copper (ZnS: Cu, Co) was considered the main phosphorescent materials. However, it has a short phosphorescence time and not stable enough during its application (Bol *et al.*, 2002). Thus new hosts are getting much attention in order to improve the long after glow properties and their stability.

Since its invention in the 19th century, the long lasting phosphor has been greatly improved. Phosphate based is particularly an attractive host because it can accommodate large concentrations of active ions without losing the useful properties of the material. It also has several special properties such as large thermal expansion coefficients, low melting temperatures, solubility and stability at higher temperatures (Day *et al.*, 1998). As example, $\text{Ca}_5\text{La}_5(\text{SiO}_4)_3(\text{PO}_4)_3\text{O}_2:\text{Dy}^{3+}$ is considered as an excellent commercial white light long lasting phosphor that has been widely applied in the development of fluorescent lamps, cathode ray tubes, field emission displays and plasma display panels (Yang and Huang, 2007).

Alkaline earth phosphates has attracted research interests in the field of photoluminescence since they are suitable hosts with high chemical stability, offers better homogeneity and lowers sintering temperature and also can produce plenty of crystal field environments imposed on emission centers. Alkali earth phosphates

constitute a wide family, which, to our knowledge, has been little explored, although their biocompatibility is well established (Liu *et al.*, 2007). The developments of phosphate based materials for a variety of technological applications, from rare-earth ion hosts for solid state lasers to low temperature sealing glasses, have led to renewed interest in understanding the structures of these unusual materials.

Over the past few decades, much attention has been devoted towards trivalent lanthanide based materials for the development of optical devices such as solid-state lasers, fiber amplifiers and infrared to visible up-converters (Walrand and Binnemans, 1998). For example, Ferhi *et al.* (2009) reported that $\text{LaPO}_4:\text{Eu}^{3+}$ has been identified as another good phosphate phosphor which displays an intense red emission under an ultraviolet (UV) source. Up to now, rare earth ion doped luminescence materials become an interesting topic in the field of luminescence material.

1.4 Statement of Problem

Among the borate, silicate and aluminate hosts materials, phosphate system seems to be the most appropriate for investigations due its lower melting temperature, higher thermal expansion coefficient and easy of fabrication techniques. However the low chemical resistance and moisture degradation of phosphate systems poses many restrictions on their commercial exploitation and usefulness. The studies by Shaw and Shelby (1988) showed various oxides such as SnO, PbO, ZnO and Fe_2O_3 improve dramatically the chemical durability. However, the addition of alkaline earth, SrO and MgO into phosphate networks is limited in structural study. Thus, this study should be useful in determining the structural properties of magnesium strontium metaphosphate system.

Even though many new long lasting phosphorescent materials are developed, the luminescence phenomenon activated by lanthanide elements remains to be explored. Besides that, most of the luminescence emissions in aluminate and silicate host material are in the ultraviolet and infrared region. Thus, in this study, magnesium strontium metaphosphate doped with Eu^{3+} and Dy^{3+} ions were studied in order to determine their luminescence properties.

1.5 Aims of the Study

The aims of this study are as follows:

1. To prepare and determine the structure and crystalline phases of magnesium strontium metaphosphate.
2. To determine the influence of the modifier concentration, MgO and SrO to the phosphate network.
3. To determine the luminescence properties of europium and dysprosium ions doped in magnesium strontium metaphosphate material.

1.4 Scope of the Study

Researches based on phosphate material are too wide. Thus, sample preparation and its characterization are controlled in this study.

1.4.1 Sample Preparation

The host material based on metaphosphate was prepared using solid state reaction method. Magnesium oxide and strontium oxide were used as modifiers in order to reduce the hygroscopic properties. In addition, Eu^{3+} and Dy^{3+} were chosen to be the dopant ions for this study in order to study the effect of dopants on the luminescence properties.

1.4.2 Sample Characterization

Different types of measurements were used in this study. The X-ray diffraction (XRD) was used to determine the phase of the obtained samples, while FT-Infrared and FT-Raman spectroscopy were used to determine the structural features of the host material. Luminescence spectra were obtained from photoluminescence spectroscopy.

1.5 Significant of the Research

We expect to obtain samples that are chemically and physically stable which can be easily prepared at lower melting temperature and lower cost compared to other host matrix material such as silicate, tellurite and aluminate. In addition, it is hoped that the doping ions; Eu^{3+} and Dy^{3+} can enhance the luminescence characteristic in magnesium strontium metaphosphate materials and glow in the visible region. These properties

contribute a lot of knowledge and a good reference for further research in developing the luminescence technology for applications of phosphor in electronics display and luminous painting.