STRUCTURAL AND LUMINESCENCE PROPERTIES OF MAGNESIUM BORO-TELLURITE DOPED EUROPIUM AND DYSPROSIUM ION CERAMIC

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To my husband, Muhammad Firdaus Ayob for your love and encouragement throughout my life

To my parents and parents in-law, for your amazing supports

To all of my professors, and teachers for their strenuous efforts in molding me into the educated person that I am today

&

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ABSTRACT

A series of xTeO$_2$-(70-x)B$_2$O$_3$-30MgO samples with $0 \leq x \leq 70$ mol% and doped samples with composition of 100-y(30TeO$_2$-40B$_2$O$_3$-30MgO)-yEu^{3+}, 100-z(30TeO$_2$-40B$_2$O$_3$-30MgO)-zDy^{3+}, and 100-y-z(30TeO$_2$-40B$_2$O$_3$-30MgO)-yEu^{3+}-zDy^{3+} with $0.2 \leq y \leq 2$ mol% and $0.2 \leq z \leq 2$ mol% were prepared via solid-state reaction method. All the samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy, Raman spectroscopy, energy dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FESEM) and photoluminescence spectroscopy. The XRD results of the samples prepared at 650^{o}C to 850^{o}C showed that the major phase was Mg(Te$_2$O$_5$) while MgTe$_6$O$_{13}$, Mg$_2$(B$_2$O$_5$) and MgB$_4$O$_7$ were observed as a minor phase. The phases of Dy(BO$_2$)$_3$, Dy$_2$Te$_4$O$_{11}$, EuB$_2$O$_4$ and Eu$_2$Te$_4$O$_{11}$ were observed in the XRD patterns of doped samples. The EDX analyses confirmed the presence of boron (B), magnesium (Mg), tellurium (Te), oxygen (O), europium (Eu) and dysprosium (Dy) elements. In addition, the weight percentage of boron (B) decreases with the increase of x mol%. Based on the FESEM images, the xTeO$_2$-(70-x)B$_2$O$_3$-30MgO samples with $0 \leq x \leq 70$ mol% prepared at 750^{o}C consist basically of sub-micron size agglomerates of irregular shape. The surface morphology of Eu^{3+}, Dy^{3+} and Eu^{3+}-Dy^{3+} doped samples is more agglomerated compared to the 30TeO$_2$-40B$_2$O$_3$-30MgO samples. The grain sizes of samples doped with Eu^{3+} (1.91 μm), Dy^{3+} (1.87 μm) and Eu^{3+}-Dy^{3+} (2.84 μm) are smaller than the grain size of the undoped sample (2.99 μm). There were six main regions observed in IR spectra which are due to the B-O-B (400-590 cm^{-1}), Te-O-Te (550 and 610 cm^{-1}), TeO$_2$ (600-800 cm^{-1}), TeO$_3$ (757 cm^{-1}), BO$_4$ (840-1200 cm^{-1}) and BO$_3$ (1300-1400 cm^{-1}) vibrations. The observed spectra also show greater bands for tellurite network with the increase of x mol%. From the Raman spectra, the intensity of the peaks due to Te-O-Te, TeO$_2$ and TeO$_3$ groups increases with the increase of x from 0 to 30 mol%. The luminescence spectra of 100-y(30TeO$_2$-40B$_2$O$_3$-30MgO)-yEu^{3+} with $0.2 \leq y \leq 2$ mol% showed that there was an increase in the emission intensity which results in the enhancement of the red emission from the samples. All the spectra of 100-z(30TeO$_2$-40B$_2$O$_3$-30MgO)-zDy^{3+} samples with $0.2 \leq z \leq 2$ mol% show the main characteristic emission lines of Dy^{3+}, which consist of magnetic dipole transition, $^4F_{9/2} \rightarrow {}^6H_{15/2}$ at 484.19 nm (blue), and hypersensitive electric dipole transition, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 578.44 nm (yellow). The observed emission spectra of 100-y-z(30TeO$_2$-40B$_2$O$_3$-30MgO)-yEu^{3+}-zDy^{3+} samples with $0.2 \leq y \leq 2$ mol% and $0.2 \leq z \leq 2$ mol% exhibit three strong bands centered at 483.78 nm, 578.97 nm and 616.83 nm which correspond to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (Dy^{3+}), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (Dy^{3+}) and $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}) transition respectively. The yellow emission ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) becomes a dominant peak in the emission spectra compared to the other emissions. The longest decay time was observed from the transition in europium and dysprosium ions.

ABSTRAK

Satu siri sampel $x$$TeO_2$-(70-$x$)$B_2O_3$-30MgO dengan $0 \leq x \leq 70$ mol% dan sampel berdop dengan komposisi 100-y(30TeO_2-40B_2O_3-30MgO)-$y$$Eu^{3+}$, 100-$z$(30$TeO_2-40B_2O_3$-30MgO)-$z$$Dy^{3+}$, dan 100-$y$-$z$(30$TeO_2-40B_2O_3$-30MgO)-$y$$Eu^{3+}$-$z$$Dy^{3+}$ dengan $0.2 \leq y \leq 2$ mol% dan $0.2 \leq z \leq 2$ mol% disediakan melalui kaedah tindakbalas keadaan pepejal. Semua sampel dicirikan menggunakan pembelauan sinar-X (XRD), spektroskopi infra merah transformasi Fourier, spektroskopi Raman, spektroskopi sinar-X tenaga menyerak (EDX), mikroskopi pengimbasan elektron pancaran medan (FESEM) dan spektrokopi fotoluminesens. Keputusan XRD bagi sampel yang disediakan pada suhu 650^oC hingga 850^oC menunjukkan fasa major ialah $Mg(Te_2O_5)$ manakala $MgTe_6O_{13}$, $Mg_2(B_2O_5)$ dan MgB_4O_7 dilihat sebagai fasa minor. Fasa $Dy(BO_2)_3$, $Dy_2Te_4O_{11}$, EuB_2O_4 dan $Eu_2Te_4O_{11}$ dilihat dalam corak XRD bagi sampel berdop. Analisis EDX mengesahkan kehadiran elemen boron (B), magnesium (Mg), tellurium (Te), oksigen (O), europium (Eu) dan dysprosium (Dy). Tambahan pula, peratus berat bagi boron (B) berkurangan dengan peningkatan x mol%. Berdasarkan imej FESEM, sampel $x$$TeO_2$-(70-$x$)$B_2O_3$-30MgO dengan $0 \leq x \leq 70$ mol% disediakan pada 750^oC terdiri daripada bentuk bergumpal yang tidak tetap bersaiz mikron. Morfologi permukaan bagi sampel berdopkan Eu^{3+}, Dy^{3+} dan Eu^{3+}-Dy^{3+} adalah lebih bergumpal berbanding sampel 30TeO_2-40B_2O_3-30MgO. Saiz butiran bagi sampel yang didopkan dengan Eu^{3+} (1.91μm), Dy^{3+} (1.87μm) dan Eu^{3+}-Dy^{3+} (2.84μm) adalah lebih kecil berbanding dengan saiz butiran sampel tidak berdop (2.99 μm). Terdapat enam kawasan dapat dilihat dalam spektrum IR yang disebabkan oleh getaran B-O-B (400-590 cm^{-1}), Te-O-Te (550 and 610 cm^{-1}), TeO_2 (600-800 cm^{-1}), TeO_3 (757 cm^{-1}), BO_4 (840-1200 cm^{-1}) dan BO_3 (1300-1400 cm^{-1}). Spektrum yang diperhatikan juga menunjukkan jalur yang lebih besar bagi rangkaian tellurite dengan peningkatan x mol%. Daripada spektrum Raman, keamatan puncak yang disebabkan oleh kumpulan Te-O-Te, TeO_2 dan TeO_3 meningkat dengan peningkatan x daripada 0 kepada 30 mol%. Spektrum luminesens bagi sampel 100-y(30TeO_2-40B_2O_3-30MgO)-$y$$Eu^{3+}$ dengan $0.2 \leq y \leq 2$ mol% menunjukkan wujudnya peningkatan dalam keamatan pancaran yang menyebabkan peningkatan pancaran merah pada sampel. Semua spektrum bagi sampel 100-z(30TeO_2-40B_2O_3-30MgO)-$z$$Dy^{3+}$ dengan $0.2 \leq z \leq 2$ mol% menunjukkan garis pancaran ciri utama bagi Dy^{3+}, yang terhasil daripada peralihan dwikutub magnet $^4F_{9/2} \rightarrow {}^6H_{15/2}$ pada 484.19 nm (biru), dan peralihan dwikutub elektrik hipersensitif, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ pada 578.44 nm (kuning). Pancaran spektrum bagi sampel 100-y-z(30TeO_2-40B_2O_3-30MgO)-$y$$Eu^{3+}$-$z$$Dy^{3+}$ dengan $0.2 \leq y \leq 2$ mol% dan $0.2 \leq z \leq 2$ mol% mempamerkan tiga jalur kuat berpusat di 483.78 nm, 578.97 nm dan 616.83 nm yang masing masing merujuk kepada peralihan $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (Dy^{3+}), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (Dy^{3+}) dan $^5D_0 \rightarrow {}^7F_2$ (Eu^{3+}). Pancaran kuning ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) menjadi puncak dominan dalam spektrum pancaran berbanding pancaran yang lain. Masa pereputan paling lama berlaku daripada peralihan dalam ion europium dan dysprosium.

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m	-	Mili
μ	-	Mikro
n	-	Nano
τ	-	Decay time
n	-	Diffraction order
θ	-	Diffracted angle of the X-ray beam
λ	-	Wavelength
S	-	Spin angular momentum
L	-	Orbital angular momentum
J	-	Total angular momentum
d_{hkl}	-	Interplanar spacing of the crystal planes
f	-	Frequency
c	-	Speed of light
h	-	Planck's constant

LIST OF ABBREVIATIONS

B_2O_3	-	Borate
B	-	Boron
H_3BO_3	-	Boric Acid
Ce^{3+}	-	Cerium ion
CL	-	Cathodoluminescence
CTB	-	Charge transfer band
CTS	-	Charge transfer state
Dy^{3+}	-	Dysprosium ion
Dy_2O_3	-	Dysprosium oxide
EDX	-	Energy Dispersive X-Ray
EL	-	Electroluminescence
Eu^{3+}	-	Europium ion
Eu_2O_3	-	Europium oxide
Er^{3+}	-	Erbium ion
H_2O	-	Water
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared
Gd	-	Gadolinium
HAB	-	Host absorption band
IR	-	Infrared
KBr	-	Kalium bromide
La^{3+}	-	Lanthanum ion
Lu^{3+}	-	Lutetium ion
LED	-	Light Emitting Diode
Mg	-	Magnesium

MgO	-	Magnesium Oxide
$(MgCO_3)_4.Mg(OH)_2.$ $5H_2O$	-	Magnesium Carbonate Hydroxide Pentahydrate
NAT	-	Sodium aluminum tellurite
NBO	-	Non Bridging Oxide
O	-	Oxygen
PbO	-	Plumbum Oxide
PL	-	Photoluminescence
Pr^{3+}	-	Praseodymium ion
RE	-	Rare Earth
SEM	-	Scanning electron microscope
Sc^{3+}	-	Scandium ion
Te	-	Tellurium
Tb	-	Terbium
TeO_2	-	Tellurium Oxide
UV	-	Ultraviolet
XRD	-	X-ray Diffraction
Y^{3+}	-	Yttrium ion
Yb^{3+}	-	Ytterbium ion

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter presents the pertinent introduction covering the brief description and a review of the materials studied. It includes the problem statement, objectives of study, scope of study, significance of study and the outline of the thesis.

1.2 Background of Study

Ceramic is defined as inorganic nonmetallic material and the atomic structure of ceramic can be crystalline, non-crystalline or partially crystalline. Typically, ceramics are very hard, brittle, high melting point materials with low electrical and thermal conductivity, good chemical and thermal stability, and high compressive strengths (Barsoum, 1997 and Minh *et al.*, 1995). Also, the ceramic can be fabricated at lower cost and in much speedy processes in a large variety of sizes and shapes (Lupei *et al*., 2005; Mohr *et al.*, 2008).

Ceramics are of tremendous interest primarily because of their wide range of applications especially in high temperature environment. They are also extensively used in fuel technology, oxygen sensor (Ciacchi *et al*., 1994), magnets ceramics (Valenzuela, 2005), all electronic equipments including integrated-chips, capacitors and digital alarms (Miller *et al*., 2002), telecommunication (Bhargava, 2005), ceramic crystal-glass (Carter and Norton, 2007). Ceramic insulators are widely used in the electrical power transmission system (Chowdhury, 2010), ceramic superconductors (David and Bruce, 1992) and other pharmaceuticals industries (Rice *et al*., 2002).

Ceramic materials can be classified into four main groups (Rajendran, 2004) that were the amorphous ceramics, which are generally referred to as glasses, crystalline ceramics, which are single phase materials like alumina, or mixtures of such materials, bonded ceramics, where individual crystals are bonded together by a glassy matrix, such as clay products and the cements, these are crystalline, and also amorphous materials.

Recently ceramic material has been study for luminescent material applications. Ceramics have the potential to become good luminescence material due to its opaque characteristic which enhances the absorption efficiency of rare earth ions (Yang *et al*., 2008). Sailaja and Reddy (2011) introduced the luminescence properties of $Eu^{3+}(MgCa)_2Bi_4Ti_5O_{20}$ and $Tb^{3+}(MgCa)_2Bi_4Ti_5O_{20}$ ceramic has shown a strong red and green emission. Ceramics can be incorporate with high concentrations of dopant ions such as rare earth and transition metal ions. The ceramic doped also have attracted much for their applications such as cathode ray tubes, lamps, X-ray detectors, electroluminescence, laser materials and fluorescent tubes (Yan *et al*., 2007 and Sastri *et al*., 2003).

Borate has been the subject of intensive investigations because of their technological and scientific importance. It offers promising choice especially for thermoluminescence applications due to its high sensitivity, low cost and easy

preparation (Krongh-Moe, 1969). Borate crystals have been used as optical materials for second harmonic generation and fluorescence. The spectroscopy of borates doped with Eu^{3+}, Pr^{3+} and Er^{3+} has been studied (Ambrosi *et al*., 1994; Thulasiramudu *et al*., 2007; Pozza *et al*., 1996). Borate has been incorporated with various types of modifier metal oxide in order to obtain the desired physical and chemical properties (Yano *et al*., 2003). In terms of luminescence, borate doped rare earth has more attention because it has high luminescence, great color coordinate and low thermal degradation (Wang *et al*., 2008).

Over the past years, the use of tellurite as a host material was focused in fundamental research and in an optical device fabrication as TeO_2 host show relatively low phonon energy. The tellurite have lower operating temperature and mostly prepared by solid state reaction method with heating temperature of 800-1000^{o}C (Kumar *et al*., 2002; Lin *et al*., 2006 and Zambelli, 2004). On the other hand, TeO_2 have been extensively studied due to good properties such as high refractive indices, good transparency, low melting point and high dielectric constant which are essential for good UV and IR transmission. Hence, TeO_2 is then very attractive and interesting for a range of different applications (Mallawany *et al*., 1992; Babu *et al*., 2007). The addition of TeO_2 into the samples may result in strong modifications of the structure as compared to that of the pure B_2O_3.

Many papers worked based on the silicate and aluminate system with higher operating temperature (Srivasta, 2009; Kuang, 2005 and Aitasalo, 2004). For the host materials, borate and tellurite also known as boro-tellurite prepared in ceramic have not been reported yet. Ceramic based on boro-tellurite host matrices doped with rare earth have applications in lasers, optical amplifier, photo sensitivity, optical storage, and bio-ceramics materials (Mallawany, 1992; Babu *et al*., 2007; Joshi *et al*., 2008; Sudhakar, 2008; Rada *et al*., 2008; Konijnendijk, 1975; Bhargava *et al*., 1987; Pascuta *et al*., 2008).

Meanwhile, adding of alkali oxide (magnesium oxide) into the host can increase the stability and chemical strength of the samples (Duverger *et al*., 1997). Also, an addition of alkali oxide has a strong influence on the luminescence properties (Dayang *et al*., 2010). Magnesium oxide doping has effectively inhibit grain growth in ceramics and it can improve the fracture toughness (Hussin *et al*., 2009). Also, magnesium oxide is well-known for its luminescent properties which are being utilized in sensors (Li *et al*., 2003). This oxide also can be as a network former (Doweidar *et al*., 2012).

Doped rare earth (RE) ions have attracted research interests in the field of luminescence. Many researchers have been carried out in order to investigate the potential of doped rare earth ion especially Eu^{3+} and Dy^{3+}-doped boro tellurite. Eu^{3+}-doped are commonly used as red emitting materials for field emission technology and LEDs, which exhibit higher luminescence efficiency compared with other luminous materials (Oikawa and Fujihara, 2005). Meanwhile, luminescence materials doped with Dy^{3+} have drawn much interest because of its white emission. Dy^{3+} is known as a good activator due to the two dominated band in the emission spectra and its position depends strongly on the crystal field of the lattice used. Hence, luminescence materials doped with Dy^{3+} can produce white emission by adjusting the yellow to blue intensity ratio value, which can be used as potential white phosphors (Hussin *et al*., 2009). Doped materials have potential applications for phosphors, display monitor, x-ray imaging, and scintillators (Blasse and Grabmaier, 1994). Moreover, the luminescence properties of the ceramic could be improved by doping with rare earth (RE) ions as an activator.

1.3 Problem Statement

Currently, a great deal of research has been focused on rare earth (RE) doped boro-tellurite glasses owing to their extensive applications (Maheshvaran et al., 2011; Selvaraju *et al.,* 2011). But, the investigation on the luminescence properties of rare earth doped boro-tellurite ceramic is not many. In the meantime, there was limited structural information regarding effect in the boro-tellurite as the host that can be reasoned to find a good luminescence material. Thus, in this study, magnesium boro tellurite doped Eu^{3+} and Dy^{3+} present to synthesize the ceramic materials by using solid state reaction method. The investigation of structural features was important in order to study the structures changes in the undoped and doped samples. Also, the luminescence emission and decay curve induced by addition of rare earth dopant were characterized for developing a new luminescence material.

1.4 Objectives of the Study

The objectives of this study are as follows:

i. To synthesize magnesium boro-tellurite ceramic and magnesium boro-tellurite doped with Eu^{3+} and Dy^{3+} ceramic
ii. To determine the crystalline phases of magnesium boro-tellurite ceramic and magnesium boro-tellurite doped with Eu^{3+} and Dy^{3+} ceramic
iii. To determine the structural properties of ceramic in term of their vibrational band, elemental analysis and surface morphology using the IR and Raman, EDX and FESEM spectroscopy.
iv. To determine the luminescence excitation, emission and decay curve of magnesium boro-tellurite doped with various dopant of Eu^{3+} and Dy^{3+}

1.5 Scope of the Study

In order to achieve the objectives of the study, magnesium boro-tellurite ceramic and magnesium boro-tellurite ceramic doped with Eu^{3+} and Dy^{3+} ions have been prepared using solid state reaction method. The crystalline phase of the obtained ceramics was determined using x-ray diffraction (XRD). The surface morphology of the ceramics was measured using Field Emission Scanning Electron Microscope. The presence of elemental composition in the prepared samples was measured using Energy Dispersive X-Ray (EDX). Also, the vibrations mode of the prepared sample was measured using FTIR and Raman spectroscopy. The luminescence spectra and decay curves of the doped ceramics was measured using photoluminescence spectroscopy.

1.6 Significance of the Study

In this research, the significance of the study is to develop a new luminescence material that can show an enhancement of the luminescence characteristic and have a long decay time. So, this new material can produce a high potential application in solid-state lighting devices.

1.7 Outline of the Thesis

Chapter 1 gives a brief description related to the magnesium boro-tellurite ceramic and magnesium boro-tellurite doped Eu^{3+} and Dy^{3+} ceramic. Chapter 2 provides an overview of the work done on the magnesium boro-tellurite ceramic with

emphasis on its structural and luminescence properties. Chapter 3 presents some background materials on the theoretical aspect of the thesis. It also discusses about the mechanism of luminescence and the principles of X-Ray Diffractogram (XRD), Fourier Transform Infrared (FTIR) and Raman properties. Chapter 4 describes in detail the preparation of the magnesium boro-tellurite ceramic and magnesium boro-tellurite doped Eu^{3+} and Dy^{3+} ceramic. Chapter 5 presents the result, analysis and discussion for experiments on XRD, surface morphology, elemental composition of the samples, IR and Raman, luminescence and lifetime. The last chapter, Chapter 6 contains the conclusion of the study and suggestions for future work.

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