CRYSTALLINE PHASE AND SPECTROSCOPIC PROPERTIES OF COPPER-CONTAINING BOROPHOSPHATE CERAMIC DOPED WITH SAMARIUM OXIDE

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A dissertation submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science

Faculty of Science
Universiti Teknologi Malaysia

MAY 2017

Specially dedicated to

my beloved father and mother,

my lovely family members

and the three little angels

who brings me lots of laugh and love throughout my journey of education

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my appreciation to everyone who involved in contributing to this completed report. I am grateful to all the supports given to me.

First and foremost, I wish to express my sincere appreciation to my main thesis supervisor, Prof. Dr. Rosli Bin Hussin, for his heartening guidance, supervision, constant encouragement and warm-hearted care throughout the process of this report. Without his continued support and interest, this dissertation would not have been the same as presented here.

Last but not least, my deepest gratitude further goes to my lovely parents, siblings and my little nephews and niece for being with me in any situation. Their endless love, unfailing support, invaluable advice and trust do help me to overcome every circumstance during the journey of education. Finally, with my greatest feelings, I would like to thanks my friends for their helps and encouragement to enable the completion of this research.

ABSTRACT

A study had successfully been conducted to determine the effects of samarium addition on the crystalline phase and spectroscopic properties of copper-containing borophosphate ceramics with nominal composition of $10CuO{-}30B_2O_3{-}(60{-}x)P_2O_5{-}xSm_2O_3$, where $x = 0.1$, 0.3, 0.5, 1.0, 1.5 and 2.0 mol% prepared by solid state reaction. The ceramic samples had been measured by X-ray Diffraction (XRD), Fourier Transform Infrared spectrometer (FTIR), ultraviolet-visible spectrometer (UV-Vis-NIR) and photoluminescence spectrophotometer (PL). All ceramic samples are found to be single crystalline of boron phosphate (BPO_4) regardless to the Sm_2O_3 concentration used. Diffraction peak intensities, average crystallite size and lattice parameters are found to fluctuate due to the addition of Sm_2O_3. FTIR spectra showed that the addition of Sm_2O_3 to the current ceramic host has no influence to the structure features or band positions, only band intensities are observed to increase. UV-Vis-NIR spectra of Sm_2O_3 doped ceramic samples recorded five absorption peaks where the peaks' intensities increasing with increasing concentration of Sm_2O_3. Both the direct and indirect band gaps decrease gradually with the increase in Sm_2O_3 concentration while the Urbach's energy shows inverse trend. The luminescence spectra for Sm_2O_3 doped ceramic samples at the excitation wavelength of 401 nm revealed three emission peaks at 560 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) and 670 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$). The peak at 600 nm which attributed to the orange emission is found to be most prominent for all of the ceramic samples and this peak is found to be shifted slightly during the addition of Sm_2O_3. Quenching effect is identified for the ceramic host doped with 1.5 mol% of Sm_2O_3. Therefore, Sm_2O_3 at 1.0 mol% of doping is the maximum doping concentration to the current ceramic sample and the good correlation between the doping and host system suggested it to be used for developing orange LED and fluorescent display devices.

ABSTRAK

Satu kajian telah berjaya dijalankan untuk menentukan pengaruh samarium ke atas fasa hablur dan sifat-sifat spektroskopi copper-borophosphate seramik dengan komposisi $10CuO-30B_2O_3-(60-x)P_2O_5-xSm_2O_3$ dengan $x = 0.1$, 0.3, 0.5, 1.0, 1.5 and 2.0 mol% yang telah disediakan melalui tindak balas keadaan pepejal. Sampel seramik telah diukur melalui pembeluan sinar-X (XRD), infra merah transformasi Fourier spektrometer (FTIR), UV-Vis-NIR spektrometer dan fotoluminesens spektrofotometer (PL). Semua sampel seramik didapati mengandungi hanya satu fasa hablur boron fosfat (BPO_4) tidak dipengaruhi oleh kepekatan Sm_2O_3. Keamatan puncak pembelauan, saiz purata crystallite dan parameter kekisi didapati turun naik disebabkan oleh penambahan Sm_2O_3. Spektrum FTIR menunjukkan bahawa penambahan Sm_2O_3 kepada hos seramik tidak mempengaruhi ciri-ciri struktur atau kedudukan jalur, hanya keamatan jalur didapati meningkat. Spektrum UV-Vis-NIR sampel seramik yang didopkan dengan Sm_2O_3 mencatatkan lima puncak penyerapan dan keamatan puncak adalah semakin bertambah menurut pertambahan kepekatan Sm_2O_3. Jurang jalur optik didapati menurun secara beransur-ansur semasa peningkatan kepekatan Sm_2O_3 manakala tenaga Urbach pula menunjukkan sifat yang bertentangan. Spektrum luminesens bagi sampel seramik didop Sm_2O_3 dengan panjang gelombang pengujaan pada 401 nm menunjukkan tiga puncak pancaran pada 560 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) dan 670 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$). Kemuncak pada 600 nm yang disebabkan oleh pancaran oren adalah puncak yang paling menonjol bagi semua sampel seramik dan puncak ini didapati beralih semasa penambahan Sm_2O_3. Kesan pelindapkejutan dikenalpasti untuk hos seramik yang didop dengan 1.5 mol% Sm_2O_3. Oleh itu, 1.0 mol% adalah kepekatan dopan maksimum bagi sampel seramik yang dihasilkan dan hubungan yang menarik diantara rangkaian dopan dan hos mencadangkan ia digunakan untuk LED oren dan peranti pencahayaan.

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LIST OF ABBREVIATIONS / SYMBOLS

B_2O_3	-	Boron oxide
BO	-	Bridging oxygen
BO_3	-	Triangular state of boric oxide
BO_4	-	Tetrahedral state of boric oxide
Cu^{2+}	-	Copper (II) ions
CuO	-	Copper oxide
$CuSO_4$	-	Copper sulphate
$CuSO_4 \cdot 5H_2O$	-	Copper sulphate pentahydrate
FTIR	-	Fourier Transform Infrared
H_2O	-	Water
H_3PO_4	-	Phosphoric acid
IR	-	Infrared
KBr	-	Potassium bromide
NBO	-	Non-bridging oxygen
NIR	-	Near Infrared
P_2O_5	-	Phosphorous pentoxide
PL	-	Photoluminescence
PO_4	-	Tetrahedral state of phosphorous pentoxide
Sm_2O_3	-	Samarium oxide
Sm^{3+}	-	Samarium ion
SO_3	-	Sulfur trioxide
UV-Vis	-	Ultraviolet-Visible
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Chapter 1 looks at some important topics related to this current research. The topics are such as a brief background about the samarium doped copper-containing borophosphate ceramic, problem statements which led to this research, objectives of the study, scope of the study and significance of this research. Lastly, thesis outline is also presented at the end of this chapter.

1.2 Research Background

The word "ceramic" is derived from the Greek words "keramikos" which means "for pottery" and "keramos" which means any pottery, dishes and tiles that are made from clay. Ceramic is known as one of the classes of materials which can either consists of highly oriented, semi-crystalline or even fully amorphous structure. Ceramic can be said as a solid compound that is composed of at least two components, which one of them is a non-metal or a nonmetallic elemental solid whereas the other one or the rest of the components can be metals or other types of nonmetallic elemental solids. In other words, ceramic is one of the classes of materials which comprised mostly inorganic nonmetallic elements as its essential component. Ceramic can be fabricated from its solid components by the application of heat at certain temperature although sometimes required both heat and pressure in order to remove any defects, such as cracks and porosity (Chiang *et al.*, 1997;

Barsoum and Barsoum, 2003).

Nowadays, ceramic has attracted a lot of attention from the worldwide researchers and becoming a popular subject in invention due to its exceptionally properties or large combinations of properties which are not feasible in other class of materials. These properties can be such as weak or strong, brittle or tough, opaque or transparent, poor electrical conductor, semiconductor or superconductor, nonmagnetic or magnetic, low melting or high melting point, porous or dense, single crystal or polycrystalline, crystalline or amorphous, and along with other properties such as high durability, water resistance, heat refractory, thermal resistance and chemically stable. Furthermore, ceramic material with various shapes and colours are also able to be fabricated, which this has leads to giving a medium for assorted creation. Also, experience has shown that ceramic materials may have their unique microstructures and therefore different morphological ways and arrangement. Crystal phases formed may also vary in morphology and appearance due to their particular structures which depending on the crystal growth and nucleation. These advantageous combinations of structural, thermal, chemical, mechanical, electrical and optical properties of ceramic material is said to be a wonderful class of material which can be appreciated by studying closely (Berezhnoi, 1970; Chiang *et al.*, 1997; Barsoum and Barsoum, 2003; Höland and Beall, 2012).

Due to the important characteristics of ceramic materials, a variety of application fields are applied based on this type of material. The applications of ceramic can be divided into two categories, which the first is traditional ceramic while the other one is advance ceramic. Traditional ceramic is those ceramic which are mostly formed with silicate and are more commonly meaning for those applications in the field of pottery, tiles, bricks, dinnerware, chinas, sculpture, porcelains and sanitary wares. It was later the discovery of ceramic can compose of much more and not just based on silicate can leads to many other fields of applications. This discovery of the ceramic by scientist and engineer is called as the advance ceramic. These other fields of applications are such as optical communication devices, lasing materials, sensors, heat sinks, ceramic insulators, electrical insulators, wires, windows, capacitors, electronic packaging, heating elements and some other applications in engineering field, such as cutting tools, valves and so on. Seeing from a combination of properties which can be hold by the ceramic and thus a various applications can be performed, the material is much depending on what types of components had been used during fabrication. Therefore, the components and their respective percentage concentrations to prepare ceramic material is important (Berezhnoi, 1970; Chiang *et al.*, 1997; Goncalves *et al.*, 2002; Barsoum and Barsoum, 2003; Höland and Beall, 2012).

Currently, boric oxide (B_2O_3) has becoming one of the most significant components in manufacturing crystalline or amorphous materials. This is due to the fact that this component possesses a combination of good properties, such as high thermal stability, good chemical durability, lower volume expansion due to the change in temperature, low melting point and good rare earth ion solubility in producing any types of materials (Kniep *et al.*, 1998; Goncalves *et al.*, 2002; Agarwal *et al.*, 2009; Bindu *et al.*, 2015). Besides that, it was found that boric oxide in glass-ceramic and ceramic materials exhibit large neutron absorption cross section which can improve the radiation stability and, thus, the application such as stabilizing the nuclear wastes is one of its recent developments (Karabulut *et al.*, 2011; Karabulut *et al.*, 2015b). The other applications of those glass-ceramics and ceramics which consisting boric oxide is such as sensors, light emitting devices, display devices, optical fibres and so on. Besides that, boric oxide is acted as a good host for dopings, which including transition metal ions and rare earth ions, making them suitable for optical and luminescence material. The only drawback of boric oxide in fabrication is degrades when react with water and exhibit lower chemical durability when acted solely (Chiang *et al.*, 1997; Shelby, 2005).

Phosphorous pentoxide (P_2O_5) is another good host component in fabrication of glass-ceramic or ceramic materials. It exhibits high ultraviolet transmission, high chemical durability and excellent physical properties, such as high thermal expansion coefficients, low melting temperature and low softening temperature. Thus, phosphorous pentoxide has been used in various applications including the laser hosts, vitrification of nuclear waste, fluorescent display devices, optical amplifiers and so on (Chiang *et al.*, 1997; Bindu *et al.*, 2015; Karabulut *et al.*, 2015a; Karabulut *et al.*, 2015b). Unfortunately, the poor chemical durability and hygroscopy nature of the phosphorous pentoxide hampered it from further development and limits its applications. Hence, it is suggested to add with another oxide in order to enhance its chemical durability (Bindu *et al.*, 2015; Karabulut *et al.*, 2015a).

In order to overcome the limitations of both boric oxide and phosphorous pentoxide, the combination of these two components is found to possess greater chemical durability compare to pure boric oxide and pure phosphorous pentoxide. This combination is called as borophosphate and it has been applied in various applications especially in optical and luminescence technology. Both percentage concentrations are considered as well. Their concentrations were suggested at high percentages due to the fact that at low concentrations may induce the glass formation ability whereas high concentrations have been found to possess the tendency in nucleation. Hence, boric oxide and phosphorous pentoxide are set at 30 and 60 mol%, respectively (Torrers *et al.*, 2006; Demirci and Günay, 2011; Sharmin *et al.*, 2013).

Other than the host components, copper oxide is also introduced into the system and act as nucleating agent by promoting and controlling the crystallization during the fabrication of ceramic. It may produce colour to the ceramic material due to its incompletely filled d orbital and, thus, acted as colouring agent in the system as well. Several studies had been conducted in order to identify its effects to the colouring, crystallization and bonds formation in the ceramic system. It was found that different concentration of copper oxide may produce different range of colours, and increasing amounts of it may promote the crystallization. Hence, according to previous research, 10 mol% of copper oxide is suitable and had been proposed in this present research (Bobkova *et al.*, 2007; Chanshetti *et al.*, 2011; Kashif and Ratep, 2015a; Rao *et al.*, 2016).

In order to introduce and enhance it's optical and luminescence properties, ceramic materials are usually doped with other elements, such as the rare earth (RE) ions. The rare earth elements consists 4*f* orbital which is then making these element exhibit a plenteous number of absorption and emission bands. Subsequently, rare earth elements acting as the active center in the host matrix are known to possess lots of fluorescing states and wavelengths available for the transitions between energy states. Therefore, the ceramic material doped with rare earth element is considered as a good luminescence host material for the applications such as fluorescence displays, lighting devices, solid-state lasers, sensors and so on (Goncalves *et al.*, 2002; Cotton, 2006; Bindu *et al.*, 2015).

Recent developments in the optical and luminescence devices have heightened the need for searching other suitable host matrices doped with rare earth element as the active center for the applications such as laser hosts, optical amplifier, fluorescence display devices and some other light sources. In rare earth family, samarium is one of the most appealing members and act as a powerful emitting center in various ceramic hosts due to its intense emissions in visible region, especially the strong emission in orange spectral region and subsequently making it suitable for the applications such as colour displays and with the possibility in forming new colour of light emitting diodes. Moreover, samarium ion has its 4*f* orbital been greatly shielded by 5*s* and 5*p* shells and consequently protecting samarium ion from any outer influence. This making samarium ion to exhibit high fluorescence efficiency and it also showing high quantum efficiency which is suitable for visible laser applications (Berezhnoi, 1970; Li *et al.*, 2007; Sailaja *et al.*, 2013). To date, these components have attracted lots of interests in the field of material science and, thus, further explore should be carried out.

1.3 Problem Statement

Although borophosphate is well-known host matrix in developing various great optical and luminescence characteristics lighting devices, however, several properties of this host matrix in ceramic system influenced by the concentration of Sm^{3+} ions are not detailed. This including the crystal parameters, such as interplanar spacing, average crystallite size and lattice parameters, of the crystalline phase formed in the borophosphate ceramic system is not fully understood and the changes of those crystal characteristics due to the influence of the Sm^{3+} ions doping concentration are also not reported yet. Furthermore, the structural features of each of the sample doped at different concentration of Sm^{3+} ions are not well established. Moreover, the optical band gaps of the borophosphate ceramic are not fully examined and the Urbach's energy is not included in most of the reports. In addition, the excitation of the Sm^{3+} ions is not well identified and the emission due to the various doping concentrations is not detailed. Besides that, none of the borophosphate host matrix has found to incorporate copper oxide as the nucleating agent in the ceramic system. Therefore, this present study aim to determine the effects of the Sm^{3+} ions at different concentrations to various properties of copper-containing borophosphate ceramic, such as crystalline phase and the related parameters, structural features, optical and luminescence properties. Hence, it is remained challenging to explore the effects on the copper-containing borophosphate ceramic doped with variation concentration of Sm^{3+} ions.

1.4 Objectives of the Study

The objectives of this research are:

(i) To determine the influence of the Sm^{3+} ions at different concentrations to the crystalline phase of the copper-containing borophosphate ceramic.

(ii) To determine the effect of Sm^{3+} ions at various concentrations to the structural features of the copper-containing borophosphate ceramic.

(iii) To determine the doping concentration effect of Sm^{3+} ions to the optical properties, such as optical band gaps and Urbach's energy, and the luminescence properties of the copper-containing borophosphate ceramic.

1.5 Scope of the Study

In this current research, the copper-containing borophosphate ceramics doped with different concentrations of Sm^{3+} ions were prepared by solid state reaction. These ceramic systems were based on the chemical composition of $10CuO-30B_2O_3-(60-x)P_2O_5-xSm_2O_3$, where $x = 0.1$, 0.3, 0.5, 1.0, 1.5 and 2.0 mol%. These concentrations of the Sm^{3+} ions were doped accordingly to the copper-containing borophosphate ceramic and were replacing the phosphorous pentoxide in the system. The manipulating variable in this research is the Sm^{3+} ions in order to determine its effect to the characteristics of the samples, such as on the crystalline phase, structure features, optical properties and luminescence characteristics.

Several characterizations had been carried out. X-ray Diffraction (XRD) technique was carried out to determine the presence of the crystal phase in the samarium doped copper-containing borophosphate ceramics while the Fourier Transform Infrared spectroscopy (FTIR) was used for the structural features determination. Besides that, an ultraviolet-visible spectroscopy in the wavelength region of near-infrared (UV-Vis-NIR) was also conducted to report the absorption spectra, which are then able to determine the optical properties of the samples, such as optical band gaps and Urbach's energy. Furthermore, photoluminescence spectrophotometer (PL) was performed in order to determine the effect of the doping concentration to the excitation and emission spectra of the copper-containing borophosphate ceramic samples. From all of the results collected, the characteristics of the samples were analyzed in detail and compare with other earlier reports.

1.6 Significance of the Study

With the continuous improvement of scientific and technological progress nowadays, the recent developments in the field for searching good optical and luminescence host material in correlation with its doping are hardly to be ignored. Therefore, this research is a further enrichment of knowledge in order to understand more about the crystal phase, structural features, optical and luminescence properties of ceramic materials influenced by the addition of Sm^{3+} ions. Also, in the view of significance of Sm^{3+} doped ceramics in the luminescence characteristics, doping with different concentration of Sm^{3+} ions may help to explore new luminescence host material which is then can be used for several lighting applications. Besides that, this current research is in hope to provide a baseline data for further research. Hopefully the benefits of this present research may therefore contribute to the mankind.

1.7 Thesis Outline

This chapter had listed out six important contents, such as the brief research background about the studying on the samarium-doped copper-containing borophosphate ceramic, the gaps of this research, the objectives of the study, scope of the study and the significant of this study. Chapter 2 discusses brief manufactures and uses of ceramics and the important features of the components used for fabrication in this research, such as boron oxide, phosphorous pentoxide, copper oxide and samarium oxide. In addition, the earlier related literatures about the CBPSm ceramic samples are also discussed in terms of the results obtained.

Next, in Chapter 3, research methodology is discussed. This includes the ceramic samples preparation from raw materials and the types of characterization techniques used in this present research along with their working principles and schematic diagrams. In Chapter 4, the experimental results obtained from those characterizations are presented and analyzed in detail. The results investigated from the samples are written in categories, such as crystallographic analysis, IR analysis, UV-Vis analysis and PL analysis. Discussion for each of the categories is also highlighted in this chapter.

Finally, conclusions and recommendations are presented in Chapter 5.

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