

STRUCTURAL AND LUMINESCENCE PROPERTIES OF EUROPIUM OXIDE
AND DYSPROSIUM OXIDE CODOPED STRONTIUM BOROPHOSPHATE
CERAMICS

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To my beloved father and mother

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ABSTRACT

A series of Eu^{3+} and Dy^{3+} co-doped strontium borophosphate ceramics were synthesized using solid-state reaction method at 1000 °C for 4 hours. The influence of strontium oxide composition on structural features of the borophosphate ceramics were investigated by using FT-IR spectroscopy. The addition of higher strontium oxide composition into the host ceramics matrix leads to an increase in ceramic network polymerization due to the replacement of bridging oxygen bonds by non-bridging oxygen bonds. The crystalline phases of ceramics were characterized by X-ray diffraction (XRD). XRD pattern revealed that strontium borophosphate ceramic existed in polycrystalline structure. Optimum composition was chosen from strontium borophosphate series based on the XRD and photoluminescence analysis. Eu and Dy were used as activator to enhance photoluminescence emission. The optimum composition determined from this study is 10SrO-40B₂O₃-50P₂O₅ codoped with 2 mol% of Eu^{3+} and 1 mol% of Dy^{3+} . The result of this study shows that photoluminescence emission and UV excitation due to energy transfer occurred within Dy^{3+} - Eu^{3+} pair ions under 350 nm and 394 nm excitation separately. The energy transfer between Dy^{3+} and Eu^{3+} takes place through resonant energy transfer mechanism. The prominent emission peaks of Eu^{3+} and Dy^{3+} co-activated strontium borophosphate ceramics were 484 nm, 574 nm, 613 nm, 660 nm and 697 nm which were assigned to transition of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^4\text{F}_{9/2} \rightarrow ^6\text{F}_{11/2}$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$. Prominent hypersensitive dipole transition was affected by structural surrounding environment of activators and polycrystalline structural network. This study shows that a new polycrystalline strontium borophosphate ceramics doped with Eu and Dy is suitable for luminescent materials.

ABSTRAK

Sampel seramik berdasarkan siri strontium borofosfat berdopan Eu^{3+} dan Dy^{3+} telah dihasilkan dengan teknik tindak balas keadaan pepejal pada $1000\text{ }^{\circ}\text{C}$ selama 4 jam. Pengaruh komposisi strontium oksida terhadap ciri struktur strontium borofosfat telah dikaji dengan menggunakan spektroskopi transformasi Fourier inframerah (FT-IR). Penambahan komposisi strontium oksida yang tinggi memberi kesan kepada matriks seramik hos iaitu meningkat polimerisasi rangkaian seramik kerana penggantian dari ikatan oksigen titian kepada ikatan oksigen tanpa titian. Fasa berhablur seramik telah dikaji dengan menggunakan teknik belauan sinar-X (XRD). Corak XRD menunjukkan struktur seramik tersebut adalah struktur polihablur. Komposisi optimum telah dipilih dari strontium borofosfat seramik berdasarkan analisis XRD dan fotopendarcahayaan. Eu dan Dy digunakan sebagai dopan bagi meningkatkan pancaran fotopendarcahaya. Oleh itu, komposisi optimum yang dihasilkan dari kajian ini ialah $10\text{SrO}-40\text{B}_2\text{O}_3-50\text{P}_2\text{O}_5$ didopan dengan $2\text{ mol}\% \text{Eu}^{3+}$ dan $1\text{ mol}\% \text{Dy}^{3+}$. Keputusan kajian ini menunjukkan bahawa pancaran fotopendarcahaya dan pengujaan UV menunjukkan pemindahan tenaga dalaman pasangan ion $\text{Eu}^{3+}\text{-Dy}^{3+}$ berlaku di bawah pengujaan 350 nm dan 394 nm masing-masing. Pemindahan tenaga antara Eu^{3+} dengan Dy^{3+} berlaku melalui mekanisme pemindahan tenaga resonan. Puncak pancaran utama bagi Eu^{3+} dan Dy^{3+} mengaktifkan seramik strontium borofosfat ialah pada 484 nm , 574 nm , 613 nm , 660 nm dan 697 nm yang berasal dari peralihan elektronik ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{F}_{11/2}$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$. Transisi dwikutub hiperpeka utama dipengaruhi oleh keadaan struktur mengelilingi dopan dan rangkaian struktur polihabluran. Kajian ini menunjukkan bahawa satu seramik polihabluran yang baharu dan sesuai dijadikan bahan pendarcahaya.

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LIST OF SYMBOLS

Δ	-	Delta
ρ_{exp}	-	experimental sample density
W_a	-	weight of sample in air
W_l	-	weight of sample in liquid
ρ_l	-	air density
ρ_a	-	liquid density
$^{\circ}\text{C}$	-	Degree celsius
Mol%	-	Molecular percentage
sin	-	Sine
θ	-	Theta/degree
λ	-	Wavelength (Lambda)
\AA	-	Armstrong
Dr	-	Radius difference percentage
CN	-	Coordination number for atom and ion
Rm	-	Radius of host cation
Rd	-	Radius of doped ion
V	-	Volume
π	-	Pine
C	-	Concentration
R	-	Distance

LIST OF ABBREVIATIONS

BC	-	Before century
XRD	-	X-ray diffraction
UV	-	Ultraviolet
FT-IR	-	Fourier transform infrared spectroscopy
PL	-	Photoluminescence
LED	-	Light emitting diode
PDP	-	Plasma display panel
1-D	-	One dimension
2-D	-	Two dimension
3-D	-	Three dimension
NBO	-	Non bridging oxygen
Ln	-	Lanthanide
nm	-	Nanometer
ml	-	Milliliter
cm	-	Centimeter
kN	-	Kilo newton
mA	-	Mili ampere
CCD	-	Charge couple device
JCPDS	-	Joint Committee on Powder Diffraction Standard

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- Appendix A - Calculation of density
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CHAPTER 1

INTRODUCTION

1.0 Introduction

The borophosphate has been investigated in recent decade. Several of studies on certain element have been carried out such as luminescence, structural, physical, and many else. Though, the research still need to be carried out for exploring the undiscovered fact of borophosphate. To study in details, several instrument were applied for obtaining data and results. Analysis in particulars to complete the research.

1.1 Background of Study

Ceramic is one of the early industries on this planet. The Archeologists have exposed human-made ceramics that belong to at least 24,000 BC. The word "ceramic" originates from the Greek word, which means "for pottery". Ceramics are highly crystalline with some glassy phase. They are basically formed by compaction of powders and fusion at high temperature ranging below melting point and then subsequently cool down to room temperature (Wagh *et al.*, 2004). Ceramics are mostly produced by using sintering, a process to transform the porous powder compact into a dense ceramic body (Tong *et al.*, 1996). However, complexity of sintering process of ceramic will cause phosphor ceramic facing difficulty in obtaining the desire shape (Fu *et al.*, 2001).

There have several categories of ceramics, which are structural, refractories, whitewares, and technical ceramic. Scientists nowadays are focusing their scope in developing ceramics that can be used in advanced material field or technical categories ceramics such as biomedical implants, phosphor, and so on. Ceramics always contain some amount of initial components or other solid phases (Maltsev *et al.*, 2004). They were possessing improved mechanical properties, offer wide range of compositions, lower cost of fabrication, less wasted material, and near net shape forming methods as compared to single crystal oxides (Seeley *et al.*, 2012).

Borate, B_2O_3 , is well known functions as good glass network former (Thulasiramudu *et al.*, 2006). Boron can form a large variety of compounds because of the complexity of the structures involved. Borate has low melting point and high thermal stability, good optical material, high luminescence that it is usually used for the formation of dielectric, plasma display panel, and cathode ray tube (Kumar Mithlesh *et al.*, 2011; Sumalatha *et al.*, 2011). By Raman spectroscopy the borate glass was found containing different dominant structural units such as boroxol rings, pentaborate, diborate and metaborate (Souza Filho *et al.*, 2000).

Phosphate, another popular host material, it is inorganic material and in their crystalline form. Phosphate is important in optical technology and industry due to their functions as application such as lamp industry, colour display and X-ray imaging. Phosphate is useful in many industries because of their luminescent, dielectric, semiconductive, catalyst, fluorescent, ion exchange properties, high absorption in VUV-UV region, moderate phonon energy, and large band gap (Lin *et al.*, 2014; Makram Megdiche *et al.*, 2014). Phosphate could be exists in crystal, glass or ceramic form. Phosphate ceramics are always used in biomedical and dentistry field due to bioactivity and non-toxicity (Omer Kaygili *et al.*, 2013). However, practical application of phosphate is limited by reason of poor chemical durability (Karabulut *et al.*, 2001). With the addition of other oxides, the chemical stability of the phosphate glasses could be greatly improved, because the added cations connect the layers or interlink the chains in the phosphate network system, leading to the formation of three-dimensional network system (Yang *et al.*, 2012).

Borophosphates, containing BO_3 , BO_4 , and PO_4 groups as basic structural units, have drawn attention since several decades due to their wide use as phosphors, lasers and non-linear optical materials (Duan *et al.*, 2006; Zhang *et al.*, 2010b). Addition of small amount of B_2O_3 into phosphate network leads to the formation of BO_4 groups that cross-link neighbouring phosphate chains, which significantly improve the chemical durability of phosphate. Therefore, borophosphate possess higher chemical stability, chemical durability and thermal stability compared with pure borate and pure phosphate (Hiromichi Takebe *et al.*, 2006; Koudelka *et al.*, 2003; Leong *et al.*, 2013; Leong *et al.*, 2014; Ren *et al.*, 2013).

Alkaline earth was commonly applied as modifier due to these oxides are able to shift up the boroxyl rings and the active group in the mixture to form tri- and tetra-bond on the host (Yasser Saleh Mustafa Alajerami *et al.*, 2012). Strontium borophosphate owning strontium oxide Sr^{2+} cations, act as network modifiers, in the structure network for breaking bridging oxygen bond to form non-bridging oxygen (NBO) bond (Sumalatha *et al.*, 2011). Strontium borophosphate having a crystallite form, SrBPO_5 , corresponding to mineral stillwellite has been investigated in detail in recent years (Lu *et al.*, 2005). SrBPO_5 contain central three single chains of BO_4 tetrahedron and linked to terminal PO_4 tetrahedron to form the system network (Liang *et al.*, 2002). Another crystallite form of strontium borophosphate is $\text{Sr}_6\text{BP}_5\text{O}_{20}$ as boron added into $\text{Sr}_2\text{P}_2\text{O}_7$ with the composition of 2SrO , $0.84\text{P}_2\text{O}_5$, and $106\text{B}_2\text{O}_3$ (Katsuo Murakami *et al.*, 1979). Strontium borophosphate related phosphor can be commonly used for mercury free lamp, plasma display panel (PDP), and tricolor lamp (Lu *et al.*, 2005; Qin *et al.*, 2010).

Phosphors are the luminescent material, which is referring to a substance that shows the luminescence phenomenon. Most of the phosphors are inorganic materials consists of a host lattice with purposely doped with transition metal or rare earth. In another words, phosphor is a substance that irradiates light by absorbing light from the sunlight and artificial light and then exhibit photoluminescence emission (Murazaki *et al.*, 2003; Ronda *et al.*, 2007). Photoluminescence is the spontaneous emission of light from a substance under optical excitation. In recent years,

phosphors containing rare-earth ions have received increasing attention due to their technological importance (Huang *et al.*, 2008).

Rare earth doped alkaline earth borophosphate lattices has been studied extensively because it has high luminescence, moderate synthetically temperature, and low thermal degradation (Wang *et al.*, 2008). Eu^{3+} ion is a suitable activator for developing desired red emission phosphor and widely used in many applications (Han *et al.*, 2013). Meanwhile, Eu^{3+} is also sensitive to the local structure which means that activator ions would have covalent interaction with surroundings anions (Bhaskar Kumar *et al.*, 2009; Huang *et al.*, 2013; Zambelli *et al.*, 2004). Dy^{3+} , another rare earth, has normally been used as high efficiency activator and it has two intense bands in the visible emission spectrum, yellow band (574 nm) and blue (480 nm) band (Jayasankar *et al.*, 2004; Kiran *et al.*, 2013; Nagpure *et al.*, 2009). Luminescence spectrum of Dy^{3+} ion was slightly influenced by the surrounding ligands of the host material, because electronic transitions of Dy^{3+} involve only redistribution of electrons within the inner 4f sub-shell (Kartik *et al.*, 2012). The luminescent materials doped with Dy^{3+} ion are commonly used for generation of white light in glass and this white colour emission luminescence glass has several advantages such as homogenous light emission, lower production cost, long lifetime, lower energy consumption and many more (Kiran *et al.*, 2013).

Zhang *et al* have successfully to synthesized the Eu^{2+} and Ce^{3+} codoped strontium borate glasses that showing strong fluorescent emission at 350 nm (Zhang *et al.*, 2006). Yasser *et al* 2012 was reporting in detail about the Dy^{3+} and Sm^{3+} doped lithium magnesium borate glasses and the emission spectra showing strong emission at 588 nm and 600 nm respectively. Polycrystalline $\text{SrB}_4\text{O}_7:\text{Eu}^{2+}$ has been prepared in the air or even in pure oxygen atmosphere, Eu^{2+} remains to be the dominating ion (Pei *et al.*, 2000). Aleksandrovsky *et al* found that the nearest environment of Eu^{3+} ions in strontium tetraborate glass differs from that in strontium borate polycrystal (Aleksandrovsky *et al.*, 2005). Liang *et al* are claimed that Tb^{3+} , Mn^{2+} codoped zinc strontium phosphate having energy transfer from Tb^{3+} to Mn^{2+} which has proven by increasing the MnO content and mean duration time of Mn^{2+} was decreased (Liang *et al.*, 2011). In the photoluminescence studies of

$M_5(PO_4)_3F(M=Ca, Sr, Ba):Dy^{3+}$ and Eu^{2+} phosphors, photoluminescence spectrum was revealed that the Dy^{3+} gives blue, yellow, and red emission at 348 nm excitation and it is predominant at $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition (Nagpure *et al.*, 2009). Qin *et al* found that Sm^{2+} ions are relatively large for ninefold-coordinated site in Sm^{2+} doped $Sr_6BP_5O_{20}$ (Qin *et al.*, 2010). Luminescence properties of Ce^{3+} doped $MBPO_5$ ($M= Sr, Ba$) were studied by Berezovskaya *et al.* It was found that the total crystal field splitting of Ce^{3+} 5d configurations are preferable to occupy the ninefold-coordinated in $MBPO_5$ ($M=Sr, Ba$), nevertheless the lowest 5d state of Ce^{3+} is at high energy due to the high degree of ionicity of the M-O bond (Berezovskaya *et al.*, 2005). Kumar *et al* measured the life time decay of Eu^{3+} doped $SrBPO_5$ and this decay spectra showed that Eu^{3+} ions are present at two different sites and mainly occupy Sr^{2+} sites (Kumar Mithlesh *et al.*, 2013).

1.2 Statement of Problem

Borate and phosphate ceramics were commonly used in bioceramic or enameling. Despite of that, borophosphate was mostly acted as host in glass network instead of ceramic and investigations on borophosphate vitreous system were almost saturated. A study on polycrystalline borophosphate or borophosphate ceramics is highly necessary for the understanding and obtaining knowledge in ceramics.

Besides that, phosphate network is very hygroscopic and chemically unstable, in general, which limits their usefulness. Since phosphate network existed in borophosphate network, chemical durability of borophosphate is still unsatisfied unless an optimize composition was determined. The chemical bondings and functional groups exist in host matrix are important to get the whole picture of structural network and also the local symmetry or coordination in borophosphate system. However, structural characteristics of borophosphate ceramics have not been detail investigated in recent years.

In last decades, many studies on luminescence of borophosphate phosphor were carried out but those studies were mainly focused on phosphor doped with Eu^{2+} , Sm^{2+} , and Ce^{3+} ions. Luminescence studies would be helpful in comprehends photoluminescence mechanism of activators and the energy transfer band for codoping situation. As far as concerned, study on luminescence properties of Eu^{3+} and Dy^{3+} codoped borophosphate ceramic that possessing polycrystalline structure has not much been carried out.

The relationship between the crystal structural system and PL emission had been reported by several researchers. However, the polycrystalline is differs from single crystal and symmetrical of this type of solid state form does vary with certain compositions. The influences of polycrystalline structural system to the photoluminescence (PL) mechanism of strontium borophosphate ceramic are still remains to be poorly known and a detailed analysis about this impact has not been established. Moreover, doubtfulness of addition of activators concentration into host network has modified structure network should be clarified in this study. There are very limited reports on Eu^{3+} and Dy^{3+} codoped ceramics. A detailed study on Eu^{3+} and Dy^{3+} codoped borophosphate ceramics will be carried out yet the results will be presented and analysed in details.

1.3 Objectives of Study

The objectives of this study are:

- i) To synthesize and determine crystalline phase of Eu^{3+} and Dy^{3+} codoped strontium borophosphate ceramics
- ii) To determine vibrational bonding and functional groups of Eu^{3+} and Dy^{3+} codoped strontium borophosphate ceramics
- iii) To determine the strongest photoluminescence intensity and photoluminescence mechanism of Eu^{3+} and Dy^{3+} codoped strontium borophosphate ceramics

1.4 Scope of Study

The ceramics sample were synthesized using sintering method and its solid state phase would be determined. XRD is employed to recognize the crystalline phase solid state sample such as amorphous, polycrystalline and crystalline structure. Besides that, identification of crystalline phase could be used to deduce the surroundings environment of activator in the sample therefore determine the optimized composition of ceramics which would give the best enhancement to photoluminescence emission.

FT-IR study is used to determine the chemical bonding and vibration bands. FT-IR measurement can detect both phosphate and borate structural bonding efficiently. However, overlapping of borate and phosphate bonding occurred in FT-IR measurement causes difficulties in identifying actual vibrational bonding position. Thus, FT-IR study combine with XRD spectra to determine the actual bonding exist in host lattice due to XRD are complimentary technique in studying structural properties.

Photoluminescence (PL) spectroscopy is essential instruments used to measure the fluorescent emission of the sample under certain excitation energy provided. In addition, PL excitation spectra could be combined with PL emission spectra to reveal the PL mechanism based on the energy transfer and defect condition in host lattice.

1.5 Significant of Study

This study has developed a novelty Eu^{3+} and Dy^{3+} codoped borophosphate ceramics. Ceramics own polycrystalline structure that having better chemical durability and stability compared with amorphous glasses. Instead of glasses, ceramic production cost is lower because it using lower temperature than host

compound melting point. An optimum composition was determined to achieve the finest and strongest emission.

Variation of structural system leads to the predominant fluorescent emission shifted. Influences of structural system to the luminescence properties were clarified clearly and this influences or modifications can be taken in consideration on developing luminescent material for industrial uses. The developed ceramic can be utilized as solid state lighting such as light emitting diodes (LED), tri-colour fluorescent lamp, plasma display panels (PDP), and field emission displays.

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