

**OPTICAL PROPERTIES OF YTTERBIUM ION DOPED PHOSPHATE
GLASS PREPARED BY SOL-GEL METHOD**

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PREPARED BY SOL-GEL METHOD

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To my beloved mother and father

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ABSTRACT

Series of $P_2O_5-Al_2O_3-Na_2O$ doped $YbCl_3$ glasses have successfully been prepared by sol-gel method. The amorphous nature of glasses are characterized using X-ray Diffraction (XRD) technique while the actual glass composition is determined using the Energy Dispersive of X-ray Analysis (EDAX). Meanwhile, the optical energy gap (E_g), Urbach energy (ΔE) and the refractive index of glass are studied using UV-Visible Spectroscopy in the wavelength range of 200nm-800nm. The glass transmission characteristic has been investigated using Infrared (IR) and Raman Spectroscopy. It is found that all glasses are amorphous in nature with composition is largely dominated by the amount of P_2O_5 . It is also found that the energy gap, E_g increases from 3.30eV to 3.50eV as the Yb^{3+} content is increased. On the other hand, the Urbach energy, ΔE lies in the range of 0.58eV to 0.21eV, decreasing with the increasing of Yb^{3+} content. Furthermore, the refractive index reduces from 1.43 to 1.41 by the addition of Yb^{3+} and almost constant as the amount of Yb^{3+} is about 1.7 mol % or more. The changes of E_g , ΔE and refractive index with the increasing amount of Yb^{3+} dopant content can be understood in terms of the changes in glass network. The IR and Raman Spectroscopy studies revealed that the glass exhibits seven vibration modes which are due to P=O vibration, PO_2 asymmetric stretching vibration, $\nu_{as}(PO_2)$, PO_2 symmetric stretching vibration, $\nu_s(PO_2)$, the $\nu(PO)$ groups, the ν_{as} of POP groups, the ν_s of POP groups and the deformation mode groups of the AlO and NaO vibration. The IR and Raman spectra show no significant distortion of the phosphate groups with Yb^{3+} ions doping level.

ABSTRAK

Sistem kaca berasaskan $P_2O_5-Al_2O_3-Na_2O$ yang didopan $YbCl_3$ telah berjaya disediakan menggunakan teknik sol-gel. Sifat amorfus kaca dikenalpasti menggunakan teknik Pembelauan Sinar-X (XRD) manakala komposisi kaca diukur dengan menggunakan Analisis Tenaga Sebaran Sinar-X (EDAX). Sementara itu, jurang tenaga (E_g), tenaga Urbach (ΔE) dan indeks biasan kaca dikaji menggunakan Spektroskopi UV-Vis dalam julat panjang gelombang 200nm-800nm. Ciri-ciri mod getaran kaca telah ditentukan menggunakan teknik Spektroskopi Inframerah (IR) dan Raman. Didapati semua kaca adalah dalam keadaan amorfus manakala kandungan kaca menunjukkan sebahagian besarnya dikuasai oleh kandungan fosfat. Kajian menunjukkan bahawa jurang tenaga, E_g meningkat dari 3.30eV hingga 3.50eV dengan penambahan ion Yb^{3+} . Sebaliknya, tenaga Urbach, ΔE didapati berkurangan dari 0.58eV kepada 0.21eV dengan penambahan ion dopan Yb^{3+} . Selain itu, indeks biasan dalam julat cahaya nampak menurun dari 1.43 hingga 1.41, dengan penambahan ion Yb^{3+} dan malar pada ion Yb^{3+} adalah kira-kira 1.7mol% atau lebih. Perubahan pada jurang tenaga, tenaga Urbach, dan indeks biasan terhadap peningkatan jumlah ion Yb^{3+} boleh difahami dari segi perubahan dalam rangkaian kaca. Kajian Spektroskopi IR dan Raman mendedahkan bahawa kaca ini memiliki tujuh mod getaran yang terdiri daripada getaran $P=O$, regangan asimetri $\nu_{as}PO_2$, simetri ν_sPO_2 , simetri νPO , asimetri $\nu_{as}POP$, simetri ν_sPOP dan mod perubahan bentuk bagi getaran AlO dan NaO . Spektrum ini juga menunjukkan penambahan ion Yb^{3+} dalam jumlah yang kecil didapati tidak memberikan sebarang perubahan ketara dalam spektra.

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LIST OF SYMBOLS

n	-	Integer
λ	-	Wavelength
d	-	Distance of atomic
θ	-	Scattering angle
ρ	-	Density of glass
ρ_L	-	Density of toluene
D	-	Density of air
W_A	-	Weight in air
W_L	-	Weight in liquid
α	-	The absorption coefficient
ω	-	The angular frequency
A	-	Absorbance
L	-	Thickness of sample
\hbar	-	Plank constant
E_g	-	Energy of the optical band gap
ΔE	-	Urbach energy or the width of band tail
n	-	The refractive index of a medium

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Glasses are increasingly used as host material for solid state lasers based on rare-earth and transition metal ionic transitions. It is an amorphous (non-crystalline) solid usually formed by the solidification of a melt without crystallization [1]. The interesting facts about the glass are it acquires many unique properties such as clear, transparent and not corrode. Glass is commonly used for windows, bottles and lamp bulb.

In recent years, phosphate glasses have been of interest for a variety of applications due to their several special properties such as large thermal expansion coefficients, low melting temperatures, and solubility [2, 3]. It is also an excellent material as host due to ion exchange ability, high gain coefficient, wide band width capability and low up conversion emission [4]. Their relatively poor chemical durability makes them generally unsuitable for practical applications [5, 6]. It was suggested that the addition of one or more of Al_2O_3 and Na_2O results in the formation of Al-O-P and

Na-O-P bonds, and leads to improvement in the chemical durability of the modified phosphate glasses [6, 7, 8].

In addition, rare-earth ions doped phosphate glasses have attracted research interest since they offer better homogeneity and lower sintering temperature. Rare-earth ions doped phosphate glasses are important materials for optical applications such as lasers, sensors and optical amplifiers [9]. One of the most important interests in rare-earth doped glasses is to define the dopant environment [10]. Ytterbium is the favourite lasing ion because of the long lifetime of the excited state, the simple energy level scheme and the small quantum defect between the pump and laser wavelength.

Unfortunately, the study of rare-earth ion doped phosphate glasses by sol-gel method is very few compared to silicate [11]. The sol-gel method, possessing advantages of well controlling the stoichiometry, particle size and morphology, is a potential method for preparing inorganic materials [12]. The sol-gel method of phosphor preparation is regarded as a wet method. A kind of metal organic compounds known as alkoxides of metals is used as precursors. These metal-organic alkoxides are either in liquid form or soluble in certain organic solvents. By using an appropriate reagent, the hydrolysis and gelation can be induced to produce homogeneous gels from the mixture of alkoxides. The gels then can be baked and sintered to produce powder ceramic sample. In this study, sol-gel method is used to produce phosphate glass.

1.2 Statement of Problem

Although there have been many investigation on phosphate based glass, the optical properties of rare-earth ion (Yb^{3+}) doped phosphate glass via sol-gel method has not been fully investigated. Therefore, the present study is done in order to investigate the effect of rare-earth ion (Yb^{3+}) on the optical properties of phosphate glasses. This is very important in order to further under-study for application of phosphate glasses.

1.3 Objectives

In order to provide more information on the glass properties, the objectives of this research are:

- a) To prepare the $\text{P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}_3$ doped with YbCl_3 glass by sol-gel method.
- b) To determine the actual glass composition.
- c) To determine the density of the glass system.
- d) To characterize the optical absorption characteristics of the glass system.
- e) To determine the refractive index of the glass system.
- f) To characterize the vibrational spectroscopy of the glass.

1.4 Scope of the Study

To achieve the objectives, the study has been divided into several scopes which are:

- a) Preparation of $P_2O_5-Al_2O_3-Na_2O_3$ doped with $YbCl_3$ glass by sol-gel method.
- b) Determination of the amorphous phase of the obtained glass using X-ray diffraction technique.
- c) Determination of the actual composition of the glass using Energy Dispersive of X-Ray Analysis (EDAX).
- d) Determination of glass density by using Archimedes method.
- e) Determination of the optical absorption properties of the samples using UV-Vis Spectroscopy.
- f) Determination of the refractive index of the samples using UV-Vis Spectroscopy.
- g) Determination of the vibration modes of the prepared samples using FTIR and Raman Spectroscopy.

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