UNIVERSITI PUTRA MALAYSIA

EFFECTS OF ERBIUM OXIDE ADDITION ON PHYSICAL AND OPTICAL PROPERTIES OF WILLEMITE-BASED GLASS CERAMIC SINTERED AT DIFFERENT TEMPERATURES

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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Zinc silicate glass is an attractive host matrix for rare-earth ions because of its fine properties, primarily optical and mechanical properties, such as good chemical stability, high UV transparency, high surface damage threshold, large tensile fracture strength and good durability. Up to now most research has been carried out on soda lime silicate (SLS) glass doped with different ingredients and rare-earths, but a few researches have been carried out on willemite-based glass-ceramic prepared using waste material and doped with erbium oxide (Er_2O_3). However; using waste materials such as SLS glass as a main source for producing silicate will be economical, cheap and helpful for reducing the aggregation of waste materials from the landfill.

The main objective of this study is to determine the effect of erbium oxide (Er_2O_3) addition on physical and optical properties of willemite-base glass ceramic sintered at different temperatures. The samples were produced via melt-quenching technique followed by powdering, pressing and sintering. In the first stage the SLS glasses were crushed, grounded, and sieved to gain the expected particle size. The prepared powder was mixed with ZnO followed by melting at the temperature of 1400 °C and quenching in water to obtain fritz glass. The prepared fritz glass was crushed using mortar and pestle to the size of 63 µm. After that the prepared powder was heat treated at the temperature of 1000 °C to produce willemite. The willemite-based glass ceramic was doped with trivalent erbium (Er^{3+}) in the ($[(ZnO)_{0.5}(SLS)_{0.5}]_{1-x}[Er_2O_3]_x$) composition where x = 1-5 wt.%. At the end, the powder was pressed and different pallets were prepared and finally sintered at different temperature ranged from 500 to1100 °C. The crystal (phase) changes with different contents of Er_2O_3 and different sintering temperatures were investigated using X-ray diffraction

(XRD); the binding structure was explored by Fourier transform infrared spectroscopy (FTIR); the microstructure, morphology and chemical composition were be studied using Field emission scanning electron microscopy (FE-SEM) along with EDAX; and the optical properties was analyzed by UV-VIS spectroscopy.

The XRD results show that well crystalline willemite (Zn_2SiO_4) with the contribution of dopant (Er^{3+}) in the lattice can be achieved at the temperature of 900 °C. The XRD results also shows that rhombohedra crystalline willemite was formed by mixing ZnO and SLS glass and optimum heat treatment of 1000 °C to produce willemite-based glass ceramics, the solid-state reaction between well crystallized willemite and Er^{3+} was obtained at 900 °C sintering temperature and Er^{3+} can be completely dissolved in the lattice at this temperature. FTIR results confirmed the appearance of the vibrations of SiO_4 and ZnO_4 groups which clearly suggests the formation of the Zn_2SiO_4 phase, the compositional evaluation of the FTIR properties of the $[(ZnO)_{0.5}(SLS)_{0.5}]_{1-x}[Er_2O_3]_x$ system indicates that the presence of erbium ions affects the surrounding of the Si-O and trivalent erbium occupy their position, these agrees with the XRD data at the peak positioned at 20.29°. The most significant modification produced by the addition of erbium and the increase of the heat treatment temperature of the studied samples shows a drop in the intensity of FTIR band located at 513 cm^{-1}, which indicates that the addition of erbium oxide and increase in the sintering temperature declines the presence of SiO_4 group**.** The micro structure analysis of the samples using FESEM shows that the average grain size of samples tends to increase from 325.29 to 625.2 nm as the sintering temperature increases. Finally, the UV-VIS spectra of all doped glass-ceramics depict absorption band due to host matrix network and the presence of Er_2O_3. The results show that the intensity of the bands tends to grow by increasing the Er_2O_3 content in the range of 1-5 wt.%, and the sintering temperature in the 500-900 °C range, followed by a drop at the temperatures of 1000 and 1100 °C. By adding the Er_2O_3 content to the host network and increasing the sintering temperature from 500-900 °C , the intensity of UV-VIS bands situated between 400-1800 nm increased due to the absorption of Er^{3+}ions and the host crystal structure. The intensity of the UV bands were observed to have dropped when the sintering temperature was increased to 1000 and 1100 °C, which indicates that by going to the temperature of 1000 and 1100 °C the Er_2O_3 particles tend to produce cluster that causes the decrease in the UV absorption bands. For the sample with x=5 wt.% Er_2O_3, two strong absorption bands situated at about 1535 and 523 nm were observed. These bands were attributed to the optical transition from $^4I_{15/2}$ to $^4I_{13/2}$ and $^4S_{3/2}$ state respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KESAN PENAMBAHAN ERBIUM OXIDE KE ATAS SIFAT FIZIKAL DAN OPTIK BAGI KACA CERAMIC BERASASKAN WILLEMITE DISINTER YANG PADA SUHU BERBEZA

Oleh

GHOLAMREZA VAHEDI SARRIGANI

Februari 2014

Pengerusi: Khamirul Amin Matori, PhD

Fakulti: Sains

Kaca zink silikat merupakan hos matrik yang menarik bagi ion nadir bumi kerana sifat-sifat optik dan mekanikal yang terperinci seperti kestabilan kimia yang baik, ketelusan UV yang tinggi, ambang kerosakan permukaan yang tinggi, tegangan kekuatan patah yang besar dan ketahanan yang baik. Sehingga kini, kebanyakan penyelidikan telah dilakukan pada kaca soda kapur silikat (SLS) yang didopkan dengan bahan-bahan yang berbeza dan juga bahan nadir bumi tetapi, hanya beberapa kajian sahaja yang telah dilakukan ke atas willemite berasaskan kaca seramik yang dihasilkan daripada bahan buangan dan didopkan dengan Erbium Oksida (Er_2O_3). Walau bagaimanapun, menggunakan bahan-bahan buangan seperti kaca SLS sebagai sumber utama untuk menghasilkan silikat akan menjimatkan, murah dan berguna untuk mengurangkan jumlah bahan-bahan buangan dari tapak pelupusan.

Objektif utama kajian ini adalah untuk menentukan kesan penambahan erbium oksida (Er_2O_3) kepada sifat-sifat fizikal dan optik kaca seramik berasaskan willemite disinter pada suhu yang berbeza.Sampel yang telah dihasilkan melalui kaedah peleburan dan pelindap kejutan diikuti oleh penghasilan serbuk, penekanan dan persinteran. Di peringkat pertama kaca SLS telah dihancurkan dan diayak untuk mendapatkan saiz zarah yang dikehendaki. Serbuk yang telah disediakan dicampurkan dengan ZnO diikuti dengan peleburan pada suhu 1400 °C dan pelindap kejutan di dalam air untuk mendapatkan kaca fritz. Kaca fritz yang dihasilkan dihancurkan menggunakan lesung, alu dan pengayak yang bersaiz 63µm. Kemudian, serbuk yang dihasilkan akan disinter pada suhu 1000C untuk menghasilkan willemite. Willemite berasaskan kaca seramik telah didopkan dengan erbium trivalen (Er^{3+}) dengan komposisi ($[(ZnO)_{0.5}(SLS)_{0.5}]_{1-x}[Er_2O_3]_x$) di mana x = 1-5 wt.%. Pada akhirnya, serbuk dimampatkan dan palet yang berbeza dihasilkan dan akhirnya disinter pada suhu yang berbeza antara 500-1000 °C. Kristal (fasa) berubah

mengikut kandungan Er_2O_3 dan suhu persinteran yang berbeza yang telah dikaji dengan menggunakan pembelauan sinar-X (XRD), struktur pengikatan akan dieksplorasi oleh spektroskopi (FTIR), mikrostruktur, morfologi, dan komposisi kimia akan dikaji menggunakan pancaran medan imbasan mikroskop electron (FE-SEM) berserta dengan EDAX, dan sifat-sifat optik dan jalur sela akan dianalisis menggunakan spektroskopi UV-VIS.
Keputusan XRD menunjukkan bahawa Kristal willemite (Zn_2SiO_4) yang baik dengan sumbangan daripada bahan pendopan (Er^{3+}) di dalam kekisi boleh dicapai pada suhu 900 °C.

Keputusan XRD juga menunjukkan bahawa hablur willemite rhombohedra telah dibentuk oleh pencampuran ZnO dan SLS kaca dan rawatan haba paling optimum adalah 1000 °C untuk menghasilkan seramik kaca berasaskan willemite, reaksi keadaan pepejal antara hablur willemite dan Er^{3+} telah diperolehi pada suhu pensinteran 900 °C dan Er^{3+} boleh diserap sepenuhnya ke dalam kekisi pada suhu ini. Hasil FTIR mengesahkan kemunculan getaran kumpulan SiO_4 dan ZnO_4 yang jelas menunjukkan pembentukan fasa Zn_2SiO_4, penilaian kerencaman sifat dari sistem FTIR bagi $[(ZnO)_{0.5}(SLS)_{0.5}]_{1-x}[Er_2O_3]_x$ menunjukkan bahawa kehadiran ion erbium memberi kesan kepada persekitaran Si-O dan trivalen erbium untuk menduduki kedudukan mereka, dan ini bersetuju dengan data XRD yang puncaknya terletak pada kedudukan 20.29 °. Pengubahsuaian yang paling penting yang dihasilkan oleh penambahan erbium dan peningkatan suhu rawatan haba sampel dikaji menunjukkan penurunan dalam keamatan FTIR band terletak di 513 cm^{-1}, yang menunjukkan bahawa penambahan oksida erbium dan peningkatan dalam suhu pensinteran menolak kehadiran kumpulan SiO_4. Analisis struktur mikro sampel menggunakan FESEM menunjukkan bahawa saiz butiran purata sampel cenderung meningkat dari 325.2 ke 9625.2 nm suhu pensinteran bertambah. Akhir sekali, spektra UV-VIS semua didopkan kaca seramik menggambarkan jalur penyerapan kerana menjadi tuan rumah rangkaian matriks dan kehadiran Er_2O_3. Keputusan menunjukkan bahawa keamatan satu band cenderung berkembang dengan meningkatkan kandungan Er_2O_3 yang dalam lingkungan 1-5 wt.%, Dan suhu pensinteran dalam julat 500-900 °C, diikuti penurunan suhu pada 1000 dan 1100 °C. Dengan menambah kandungan Er_2O_3 kepada rangkaian tuan rumah dan peningkatan suhu pensinteran 500-900 °C, keamatan UV-VIS band terletak di antara 400-1800 nm meningkat disebabkan penyerapan ion Er^{3+} dan struktur hablur perumah. Keamatan satu band UV telah diperhatikan dan menunjukkan penurunan apabila suhu pensinteran meningkat kepada 1000 dan 1100 °C, yang menunjukkan bahawa dengan mengenakan suhu 1000 dan 1100 °C zarah Er_2O_3 cenderung untuk menghasilkan kelompok yang menyebabkan penurunan dalam jalur penyerapan UV. Bagi sampel ini dengan x = 5 wt.% Er_2O_3, dua band penyerapan yang kuat terletak pada kira-kira 1535 dan 523 nm telah dipatuhi. Band-band ini telah dikaitkan dengan peralihan optik dari keadaan $4I_{15/2}$ untuk $4I_{13/2}$ dan $4S_{3/2}$ masing-masing.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

m/m	Mass/mass
µm	Micrometre
4f	Atomic orbital
$5p^6$	Atomic orbital
Er^{3+}	Trivalent Erbium
Eu^{3+}	Trivalent Erupium
Tb^{3+}	Trivalent Terbium
Ce^{3+}	Trivalent Cerium
mm	Millimetre
$^4I_{13/2}$	First excited state energy level
$^4I_{15/2}$	Grand state energy level
$^{4I}{}_{11/2}$	Second excited state energy leve
h	Hour
T_g	Glass transition temperature
ms	Millisecond
$^4I_{9/2}$	Third excited energy level
$^4F_{9/2}$	Forth excited energy level
$^4S_{3/2}$	Fifth excited energy level
$^2H_{11/2}$	Sixth excited energy level
wt	Open source widget-centric
L_A	Green body dimension
L_B	Dry dimension
λ	Electron-phonon coupling constant
µ	Micro
A	Optical absorption coefficient
E_{opt}	Indirect allowed optical band gap energy
C	Constant independent of phonon energy
hν	Phonon energy
2θ	Scanning angle
ρ	Density

LIST OF ABBREVIATIONS

SLS	Soda Lime Silica
XRD	X-Ray Diffraction
FTIR	Fourier transform infrared spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
UV-VIS	Ultraviolet-visible spectroscopy
ATR	Attenuated total reflectance
EIA	Electronics Industries Association

CHAPTER 1

INTRODUCTION

1.1 Glass and glass-ceramic materials

Glass is a product of inorganic fusion obtained by cooling down the molten of inorganic materials to a rigid condition. Glasses can be synthesized in various shapes by melt quenching method. Today, the uses of glasses are far ranging with applications in the architectural, electrical and electronic devices, telecommunications and aerospace industries. Glass-ceramics are known as which include an amorphous phase and one or more crystalline phases. Glass-ceramics are produced through controlled crystallization process of the base glass in contrast to a spontaneous crystallization which is not acceptable by glass manufacturer. Glass-ceramics materials pose properties of both glasses and ceramics including the fabrication advantage of glass and special properties of ceramics. Glass-ceramics usually have crystallinity between 30% [m/m] to 90% [m/m] (Hummel, 1951). Glass-ceramics materials have properties of high strength, translucency, pigmentation, opalescence, high chemical durability, high temperature stability, low or negative thermal expansion, fluorescence, machinability, ferromagnetism, resorbability, biocompatibility, bio-activity, ion conductivity, superconductivity, isolation capabilities, low dielectric constant and loss, high resistivity and break down voltage (Holand & Beall, 2002b; McMillan, 1974). These properties can be optimized by controlling the composition of the base glass and applying a controlled heat treatment/crystallization to the base glass.

Most of the production of glass-ceramics is mostly done in two steps: firstly, a glass is produced through a glass manufacturing process such as melting and quenching. Then, the glass is reheated again at specific temperature. During this heat treatment, the glass undergoes partial crystallization. The properties of glass-ceramics are determined by the precipitation of crystallized phases from the glasses as well as their microstructure. Generally, to control the crystalinity and the type of crystal structure on the final glass-ceramics are depend on the parent glass composition, thermal treatment and the addition of nucleating agent (Hu, Li, Dali, & Mao Liang, 2005). Mostly, nucleating agents are added to the base composition of the glass-ceramics in order to control and facilitate crystallization process. Nucleation is the initiation of a phase change in a small region, such as the formation of a solid crystal from a liquid solution. It is a consequence of rapid local fluctuations on a molecular scale in a homogeneous phase that is in a state of metastable equilibrium.

1.2 **Background on sintering and sintering temperature**

Sintering is a technique used to produce substances from powders which is based on diffusion of atoms. Diffusion takes palace above absolute zero in any material however; in the elevated temperature the diffusion is much quicker. Sintering is the processes of heating the powdered material to a temperature below the melting point. During sintering processes, the atomic composition of the powdery particles diffuses across the boundaries of the particles producing a solid piece by fusing the particles together. Sintering is known as the shaping process for materials such as glass and glass-ceramic with extremely high melting points. Besides that, Sintering is part of manufacturing process of pottery and ceramic objects substances such as glass, alumina, zirconia, silica, magnesia, lime, beryllium oxide and ferric oxide. The benefits of sintering stage are, higher levels of purity and uniformity in starting materials and preservation of purity, since it has the simpler and fewer subsequent fabrication steps (Carter & Norton, 2007; Kang, 2005). Stability of the details in repeatable operations, achieved by controlling the grain size at the input stages, there are no binding contact in-between segregated powder particles as often observed in processes of melting. There are different benefit of sintering such as no deformation needed to produce directional elongation of grains, ability to achieve materials with controllable and uniform porosity, ability to obtain objects with a near net-shape, ability to achieve materials which are difficult to fabricate by other techniques, and the ability to produce highly durable material.

The higher the sintering temperature will cause glass-ceramic particles compacted. It tends to decrease the porosity and increase the density as well as the grains size of the glass-ceramic. The glass-ceramic after sintering has a higher thermal conductivity, elastic modulus and mechanical strength (Shackelford & Doremus, 2008). Besides, sintering also increases the diffusion rate and reduces the dislocation of particles. The effective sintering temperature on the microstructure of a single phase oxide is in the range of 0.75-0.90 of its melting point (Shackelford & Doremus, 2008). The effective solid-state sintering also limit to the powder with a size which is less than 10 μm. It is due to the finer powder has a greater surface area per unit volume. Consequently, it has a greater driving force to cause densification at lower temperature (Shackelford & Doremus, 2008). The effectiveness of a solid-state sintering process can also be increased by applying higher pressure, slowed the heating rate and extending the heating period. There is various mass transport mechanisms involved in the solid-phase sintering of powder. Mass transports mechanisms include surface diffusion, volume diffusion, grains boundary diffusion, viscous flow, plastic flow and vapor transport from solid surface (German, 1996).
There are three stages of solid-phase sintering that take place in the microstructure evolution. The stages of the solid-phase sintering depend on the sintering temperature, sintering period, as well as the nature of the material such as melting temperature, particle size shape and surface. By assuming all the powder particles are spherical, there are wide inter-particle placing present in them. The first stage of sintering occurred when the spherical come into contact, with a weak cohesive force within them. Small mass of particles are participated to form neck. Hence, the neck growth of particles and decreases porosity is significant in microstructure (German, 1996). The intermediate stage of sintering occurred as large mass of particles are involved into neck growth. The particles are no longer spherical because they are

interconnected. The open pore network with porosity larger than 8% becomes geometrically unstable. The pores undergo shrinkages and become smoother. In this stage, densification can be significantly observed the microstructure (German, 1996). In the final stage of sintering, the grain growth and densification are evident. Several grains are joined together and growth to a larger size. Hence, the average grain size was increased and fewer grains can be observed on a unit area in micrograph. The pores observed are spherical and closed. They are presented on the fractured grain boundaries. The total surface porosity achieved is lower than 8%. The air in the pores will limit the endpoint of the total porosity and density after sintering (German, 1996).

1.3 The concept of doping

The doping process was properly first developed by John Robert Woodyard at Sperry Gyroscope Company throughout World War II (Woodyard, 1985). Other researchers also have performed in line with his work by Teal and Sparks at Bell Labs (Sparks, 1950).

Generally, doping is the process of adding impurities to material. For instance, in the fabrication of semiconductors, the impurities are usually introduced to the host lattice to modify their electrical and optical properties. Mainly doping processes are important for the creation of electronic junctions in silicon, and for the manufacturing of semiconductor devices (Sze, 1981). In the technology of glass-ceramic phosphors materials, some of the impurities such as rare-earth elements are utilized as activators to enhance the luminescence characteristics. Such phosphors materials prepared from inorganic compounds by doping with suitable activators and impurities are capable of converting one or more forms of energy into radiation in or close to the visible region of the electromagnetic spectrum. Erbium doped materials have been widely studied for several years as Er^{3+} ions illustrate emission at 1500 nm, which coincides with the minimum-loss transmission window of silica based optical fibers telecommunication systems (Miniscalco, 1991).

1.4 Rare-earth luminescence in solid host

The rare-earth or lanthanides are the series of elements in the sixth row of the periodic table starting from lanthanum to ytterbium at the end. Rare earths are specially identified by a partially filled 4f shell that is shielded from outer field by $5s^2$ and $5p^6$ electrons. In this series, the energy levels of elements are not largely sensitive to the surrounding environment which they are in.

The rare-earth incorporated in crystalline or amorphous hosts in the form of 3+, or occasionally 2+, ions. The 3+ ions all exhibits strong narrow-band intra-4f luminescence in different hosts, and the provided shield by the $5s^2$ and $5p^6$ electrons. It means that rare-earths have radiative transitions in solid hosts similar to those of the free ions and weak electron–phonon coupling. The diagrams related to energy level of the isolated 3+ ions of each of 13 lanthanides with partially filled 4f orbitals from cerium (n=1) to ytterbium (n=13) is shown in Figures 1.1 and 1.2. Though some of the divalent species (principally samarium and europium) also

shown luminescence, it is the trivalent ions which are of mostly of highly interest. The intra-4f transitions are parity forbidden and are made partially allowed by crystal field interactions mixing opposite parity wave functions.
Therefore, luminescence have a long life time (in the range of millisecond), and narrow line widths. An intense and narrow-band emission can be achieved by chosen the suitable ions across most of the visible region and into the near infrared. The more technologically important radiative transitions are highlighted. Figure 1.3 further shows the influence of spin–orbit and crystal field interacting with the energy of the Er^{3+} ion (Kenyon, 2002).

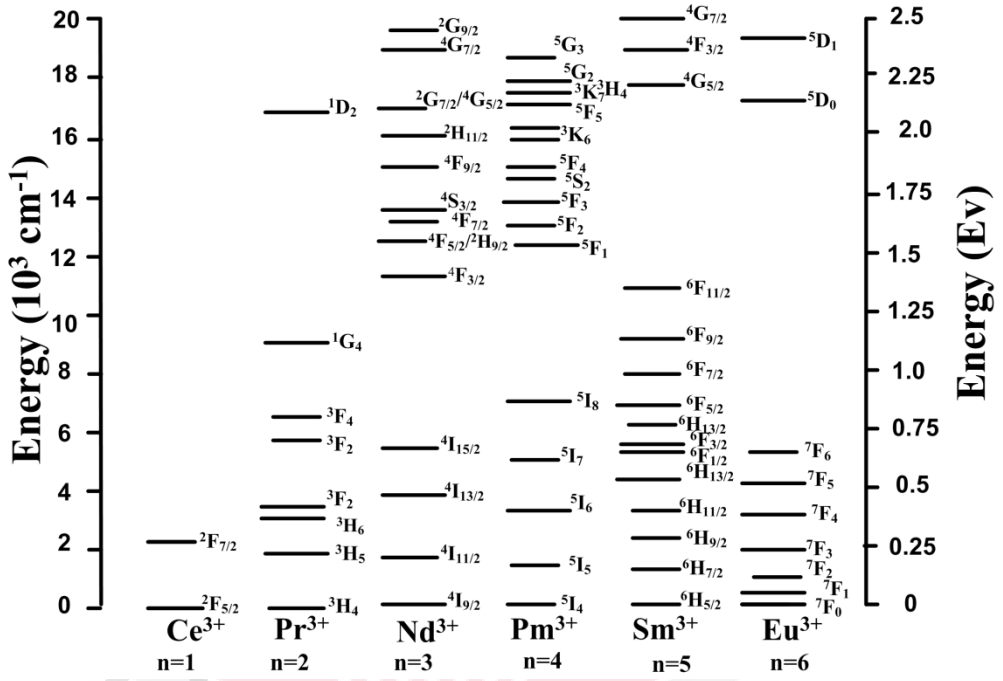

Figure 1.1 The Energy levels of the triply charged lanthanide ions, (n=1-6) (Kenyon, 2002).

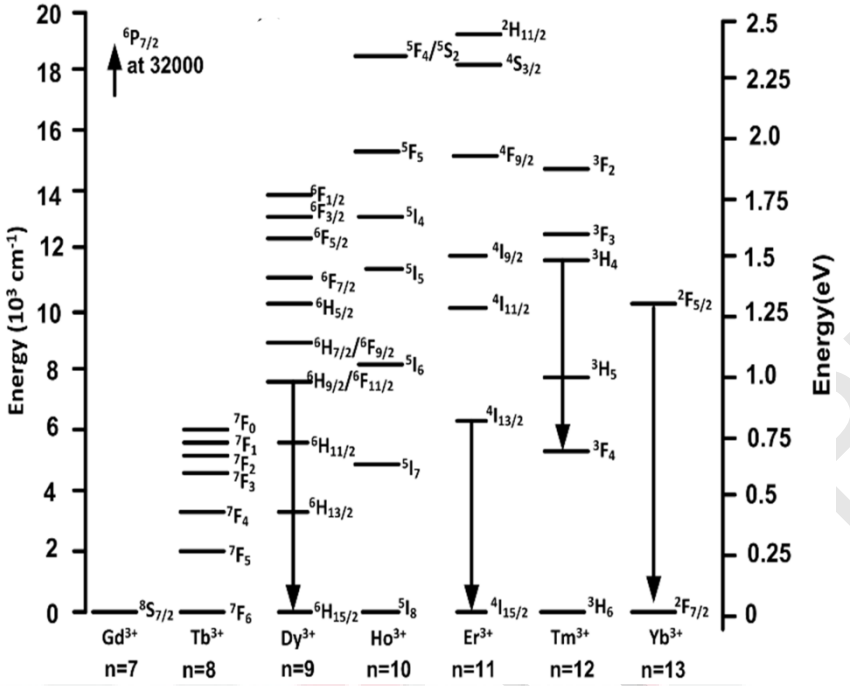

Figure 0.2 The Energy levels of the triply charged lanthanide ions, (n=7-13) (Kenyon, 2002).

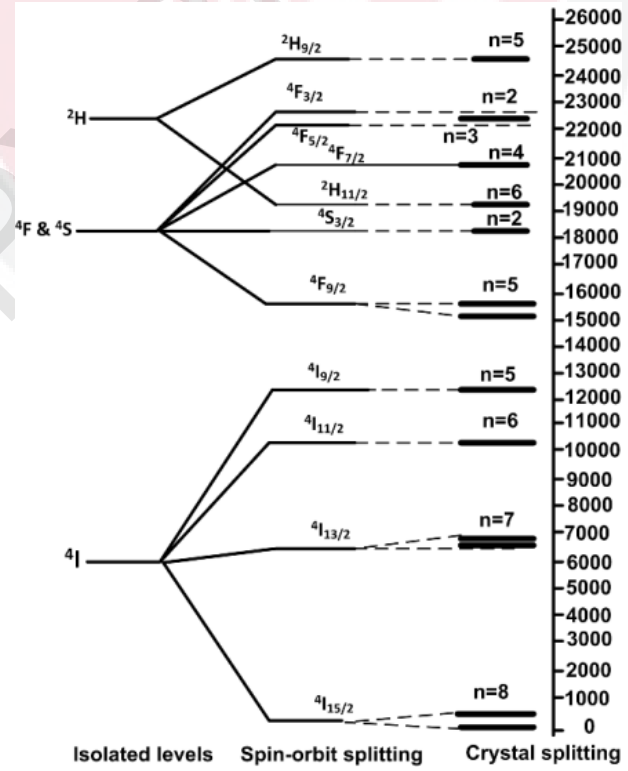

Figure 0.3 The influence of spin orbit and crystal field splitting on the energy levels of the trivalent erbium (Er^{3+}) ion in silicate host (Kenyon, 2002).

1.5 **Problem statement**

Phosphate glasses are excellent host media for the Er^{3+} ions because of their attractive spectroscopic characteristics (such as large emission cross-section and a weak interaction among active ions, which may cause concentration quenching). In present days, phosphate glasses are commonly utilized for bulk laser applications. However, they are not much suitably applicable for integrated optics purposes (i.e., planar or channel waveguides), due to their poor chemical stability and low transition temperatures (J. Yang et al., 2004). On the contrary, silicate glasses, have much better chemical stability which is important for ion-exchange techniques to fabricate optical waveguides (Capek et al., 2004). Up to now the silicate glasses such as germanosilicate (R. Santos, L. Santos, & R. Almeida, 2010; Smith, 1978), soda lime silicate (Khalil et al., 2010) soda-lime alumino silicate (Berneschi et al., 2006; Righini et al., 2005), lithium aluminum silicate (Ananthanarayanan, Kothiyal, Montagne, & Revel, 2010), and lithium silicate glasses (Du & Chen, 2012) are chosen to be suitable host for the rare-earth especially Er^{3+}. On the other hand, the knowledge of the effects of erbium on zinc silicate (willemite) especially willemite prepared by waste materials and the effects of sintering on the undoped willemite and rare-earth doped willemite sintered at different temperature are limited. In fact silicate glass-ceramics such as willemite (zinc silicate) is of much interest kind of silicate, are the semiconductors of choice for the overwhelming majority of microelectronics, and the full integration of silicates microelectronics with optical emission would allow the realization of low-cost, high-speed communication within circuits, between processors, or across local area networks (Kenyon, 2002). Moreover; nowadays, many countries are facing a difficulty in disposing solid wastes materials from industries and from man-made waste because of limited landfill sites to dump these solid wastes. In Malaysia 19,000 tons of wastes are produced every day, and a majority of that ends up in landfills. Malaysia currently has 230 landfill sights and 80% of them will reach maximum capacity within next two years and with land for landfill site being at a premium, there is going to be a big problem to ours next generation. Recycling of low cost wastes materials such as soda lime silica (SLS) glass in order to fabricate applicable material in the field of optic and telecommunication will be beneficial to reduce the large amount of solid waste produced daily (Berneschi et al., 2006). Generally SLS glass have been known for their high insulating properties (Hayashi & Kudo, 2001), good and acceptable mechanical (Wang et al., 2005), and chemical properties (Khalil et al., 2010). Also they have been used as radiation-sensitive dosimeter, especially glasses doped with transition metal ions (Mercier, Palavit, Montagne, & Follet-Houttemane, 2002) or rare-earth ions (Elbatal, Khalil, Nada, & Desouky, 2003). Beside that using waste material in the scientific felid is affordable because majority of waste material are cheap and accessible. The artificial materials which have a potential to produce glass ceramic are SLS, table salt and aluminum cans. The main framework of the SLS glass is SiO_4 tetrahedral of silica that plays an important role as network forming oxide. Pure silica has a very high melting temperature which is 1713 °C (Shackelford & Doremus, 2008) that is high temperature and unaffordable. On the other hand using waste SLS is economical because it has soda as a flux that reduce the eutectic temperature to ~800 °C at the silica-rich end of the phase diagram and the presence of SLS glass into other oxides is capable to enhance oxides interaction and crystal formation upon sintering (Shackelford & Doremus, 2008).

1.6 **Importance of the study**

Nowadays glasses and glass ceramics play a major role in telecommunication systems and they have been intensively studied for application as conversion fiber, optical amplifiers, solid-stated laser and 3-D displays. Previously most researches focused on silica oxide as a glass-forming network. Among oxide glasses, phosphate and silicate glasses are the two most important materials, and they have been used extensively for lasers and fibre amplifiers (Veasey, Funk, Sanford, & Hayden, 1999). Compared with silicate glasses, phosphate glasses are more limited in their use because they are hydroscopic in nature (J. Yang et al., 2004).and have a lower glass transition temperature. In contrast, silicate glasses exhibit superior chemical resistance and are optically transparent at the excitation and lasing wavelengths (H. Lin, Pun, & Liu, 2001). Therefore, they are more compatible with the fabrication process in the development of optical devices (Capek et al., 2004).

Various examples of rare-earths such as erbium (Er^{3+}) (R. Santos, L. F. Santos, & R. M. Almeida, 2010), europium (Eu^{3+}) (Du & Kokou, 2011), terbium (Tb^{3+}) (Pan et al., 2008), and cerium (Ce^{3+}) (Brandily, Marie, Lumeau, Glebova, & Glebov, 2010) are used as dopant for silicate glass-ceramic to produce a full color display. The usage of rare-earth ions has been remarkably used as phosphor activators. In the case of luminescent rare-earth, the attention is toward in one species trivalent erbium (Er^{3+}) with emission band around 1.53 mm. The justification for this are easy to come across when considering the rapid increase in optical telecommunication and some of the material limitations on this technology (Kenyon, 2002).

Figure 1.4 shows the loss spectrum of silica fiber. There are two low losses (or windows): in the spectrum of silicate fiber one between 1200 and 1350 nm, and the second around 1450–1600 nm (known as ultra-low-loss window). This phenomenon is caused by the combined effects of losses due to Rayleigh scattering and infrared absorption due to the Si–O species. The 1500 nm window is the wavelength region of choice for telecommunications where fortuitously coincides with the 1535 nm intra-4f $^4I_{13/2}$- $^4I_{15/2}$ transition of the Er^{3+} ion (Figure. 1.5).Therefore, there has been major interest in using erbium-doped materials to attain elements and sources in telecommunications systems. In the late 1980s, the development of the erbium-doped fiber amplifier (EDFA) (Desurvire, Simpson, & Becker, 1987; Mears, Reekie, Jauncey, & Payne, 1987) exploited the $^4I_{3/2}$-$^4I_{15/2}$ transition and permitted the transmission and amplification of signals in the 1530–1560 nm region without the need for expensive optical to electrical conversion (Kenyon, 2002).

On the other hand, willemite as particular kind of silicate glass-ceramics can also be considered as a proper host for erbium (Auzel & Goldner, 2001). Willemite has been discovered over the last 180 years and still is the most widely practically used and most interesting for hosting of rare-earth ions. Following its discovery, researchers have focused on the occurrence, crystallography, luminescence and industrial application of willemite. Up to now willemite generally has been created by pure material and by different methods such as sol-gel methods, supercritical water methods, vapor methods, and solid-state methods, also in order of using in different area, kinds of metals and rare-earths have been chosen to dope on willemite glass-ceramic (Takesue, Hayashi, & Smith Jr, 2009).

Anyway, at present there is not reported research on producing willemite by using waste materials and using trivalent erbium (Er^{3+}) as a dopant. In this work willemite as a host was produced by using waste material and trivalent erbium (Er^{3+}) was used as a dopant material.

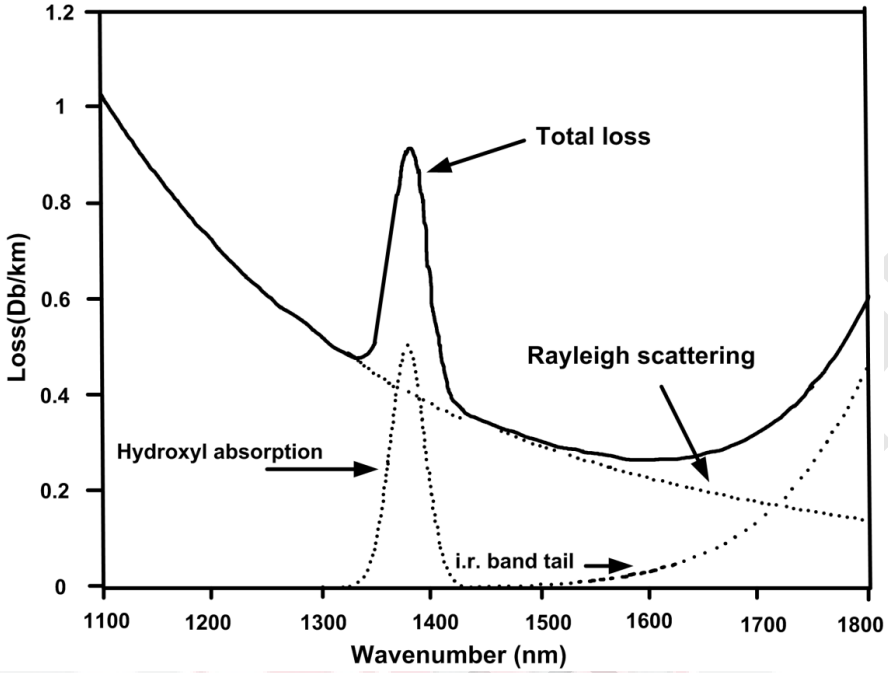

Figure 0.4 Silicate optical fiber loss spectrum in the near IR region.

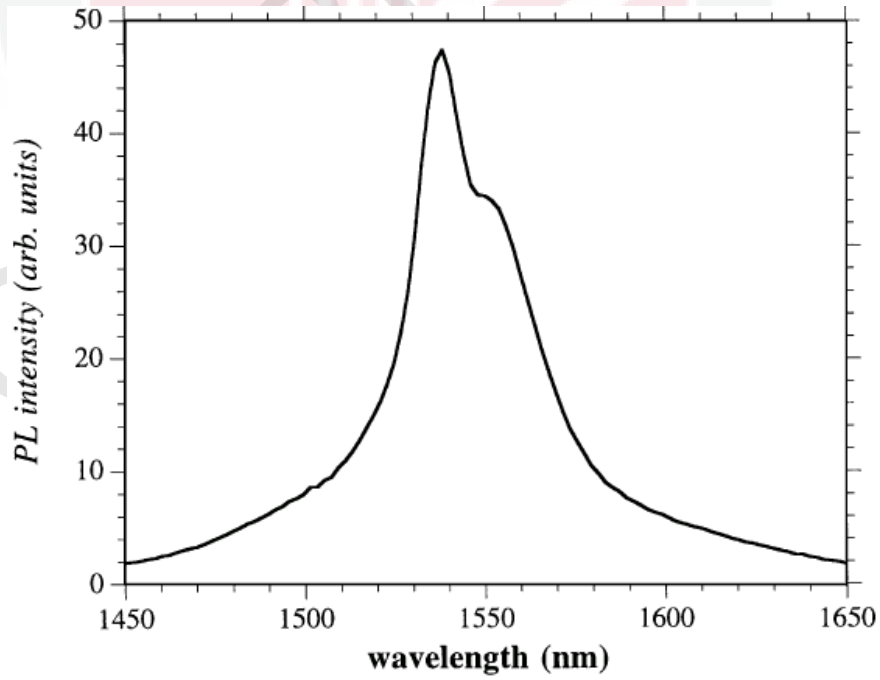

Figure 0.5 PL spectrum of Er^{3+} ($^4I_{13/2}$ to $^4I_{15/2}$) in a silica host.

1.7 Objectives of research

This study was done based on the following objectives which are mentioned below:

1. To analyze the density and linear shrinkage of willemite-based glass ceramic added with different content of Er_2O_3 and sintered at various temperature.
2. To characterize the crystal phase and microstructure of produced willemite-based glass ceramic.
3. To determine the optimum content of Er_2O_3 and sintering temperature for willemite-based glass cramic
4. To evaluate the optical properties of Er_2O_3 doped willemite-based glass ceramic utilizing ultra-visible (UV-VIS) spectroscopy.

1.8 Scope of the study

In order to attain the aims of the study, the scopes of the study as follow

1. The base of willemite with stoichiometric equation of $(ZnO)_{0.5}(SLS)_{0.5}$ produced using melting and quenching technique followed by sintering, then the willemite-based glass ceramic doped with Er_2O_3 from 1-5 wt.%.
2. Samples structure is investigated with X-ray diffraction technique to settle the crystalline structure of the glass-ceramic samples.
3. The bonding structure of samples is detailed by using Fourier transforms infrared spectroscopy (FTIR).
4. The density of obtained samples is investigated using Archimedes principle with water as the fluid medium.
5. Samples microstructure, morphology and chemical composition structure is studied using Field emission scanning electron microscopy (FE-SEM) along with EDAX.
6. The optical property of samples is investigated using UV-VIS spectroscopy.

1.9 Thesis organization

The thesis is presented five chapters. Chapter 1 presents a brief introduction into the research topic and as well as statement of the objectives of research. Chapter 2 provides a survey of the literature on glass and glass-ceramic, brief information about the (willemite preparation). Details of the experimental procedures performed in this work are presented in chapter 3Chapter 4 presents the results of XRD analysis, FTIR spectra, density and linear shrinkage, UV-VIS and Fe-SEM analysis. Chapter 5 contains conclusions and recommendations for future work and refinement that can be done.

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