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EFFECTS OF Pr6O11 ADDITION AND SINTERING TEMPERATURE ON STRUCTURAL, OPTICAL AND LUMINESCENCE PROPERTIES OF Zn2SiO4 BASED GLASS CERAMICS

NURZILLA BINTI MOHAMED

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By

NURZILLA BINTI MOHAMED

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In appreciation of their love and sacrifices, this thesis is dedicated to my family especially my beloved parents MOHAMED B. SALLEH and CHE HASNA@RAHMAH BT AHMAD and my siblings who have been giving me full moral support throughout the years.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman: Associate Professor Jumiah Hassan, PhD
Faculty: Science

In recent years, great interest was focused on glass ceramics for applications in laser, optical amplifier and optical sensor. Up to now, the commercial Zn_2SiO_4 were fabricated due to its high luminescence and chemical stability. This research highlights the alternative sources of SLS-ZnO glass in order to produce Zn_2SiO_4 glass ceramics by varying Pr concentration and sintering temperatures. The six series of Pr addition into SLS-ZnO glasses of the type $_x(Pr_6O_{11})._{100-x}(SLS_{0.5}$-$ZnO_{0.5})$ (where x = 0, 1, 2, 3, 4, at 5 wt. %) were prepared by mixing the raw materials Praseodymium Oxide (Pr_6O_{11}), Soda Lime Silica (SLS)and Zinc Oxide (ZnO) as starting materials in the appropriate amount. Then, these mixture materials were melted at 1400 ^oC for 2 hours in alumina crucibles by electrical furnace. The molten glass was poured into water by quenching technique in order to produce glass frit. The glass fritz was finely ground and sieved to be in powder form with the size of 63 µm. Density of SLS-ZnO glass increases by increasing Pr concentration. The glass system which consists of amorphous phase and more non-bridging oxygen were confirmed by XRD and FTIR analysis. The band gap fluctuated when Pr concentration is lower than 3 wt.% and enhanced at higher Pr concentration (4 and 5 wt.%). However, the luminescence intensity decreased as the Pr concentration increased from 4 to 5 wt.% may due to the concentration quenching effects.

Besides that, Pr doped Zn_2SiO_4 glass ceramics were prepared by sintering SLS-ZnO glass from 600 to 1000 ^oC. The properties of Pr addition into Zn_2SiO_4 were evaluated in terms of structural, optical and luminescence properties at different sintering temperatures. The formation of α-Zn_2SiO_4 in the SLS-ZnO host matrix is proven by XRD, FTIR, FESEM and EDX analysis. The XRD indicates the peaks of α-Zn_2SiO_4 increases in intensity with increasing sintering temperatures by increasing Pr concentration from 0 to 2 wt.% Pr. Nevertheless, the intensity of α-Zn_2SiO_4 phase decreases at 3 wt.% Pr but increases at high Pr concentration (4 and 5 wt.% Pr). The

FTIR spectra showed the presence of Zn_2SiO_4 phase in the glass ceramics network occurring at ~467 and ~697 cm^{-1} which is supported by EDX analysis. FESEM micrographs showed the grain growth increases with increasing sintering temperatures. The average grain growth decreases as Pr concentration increases from 1 to 5 wt.%. The sharpness absorption band of ~444 nm increases as Pr concentration and sintering temperatures increases which is in good agreement with the excitation of blue LED for the fabrication of White Light Emitting Diode (WLED).

The band gap increases with increasing sintering temperatures up to 900 ^oC and decreases with further sintering of 1000 ^oC due to the crystallinity of Zn_2SiO_4 phase. The substitution of Pr addition into the host matrix fluctuates the band gap when Pr concentration is lower than 4 wt.% and decreases at 5 wt.% Pr. The increase in crystallinity of Zn_2SiO_4 is suggested to be due to the enhancement of the luminescence with increasing sintering temperatures. It is interesting to note that the luminescence intensity decreases by increasing Pr concentration up to 3 wt.% to increase at 4 and 5 wt.% Pr due to the incorporation of the Pr^{3+} ion in the Zn_2SiO_4. This suggests that Pr doped Zn_2SiO_4 possess suitable structural, optical and luminescence properties and could be a promising glass ceramic material for optoelectronics devices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

KESAN PENAMBAHAN Pr_6O_{11} DAN SUHU PENSINTERAN PADA SIFAT STRUKTUR, OPTIK DAN KEPENDARKILAUAN Zn_2SiO_4 BERASASKAN KACA SERAMIK

Oleh

NURZILLA BINTI MOHAMED

Disember 2017

Pengerusi: **Prof. Madya Jumiah Hassan, PhD**
Fakulti: **Sains**

Sejak kebelakangan ini, minat yang tinggi telah difokuskan pada seramik kaca untuk aplikasi dalam laser, penguat optik dan sensor optik. Sehingga kini, komersial Zn_2SiO_4 telah direka kerana kependarkilauan tinggi dan kestabilan kimia. Kajian ini menekankan sumber alternatif kaca SLS-ZnO untuk menghasilkan seramik kaca Zn_2SiO_4 dengan pelbagai kepekatan Pr dan suhu pensinteran. Enam siri penambahan Pr kepada kaca SLS-ZnO dari jenis $_x(Pr_6O_{11})$. $_{100-x}(SLS_{0.5}$-$ZnO_{0.5})$ (di mana x = 0, 1, 2, 3, 4, pada 5 wt.%) telah disediakan dengan mencampurkan bahan-bahan mentah Praseodymium Oxide (Pr_6O_{11}), Soda Lime Silica (SLS) dan Zinc Oxide (ZnO) sebagai bahan permulaan dalam jumlah yang sesuai. Kemudian, bahan campuran ini dicairkan pada 1400 ^oC selama 2 jam di dalam mangkuk pijar alumina oleh relau elektrik. Kaca cecair dituangkan ke dalam air dengan teknik lindapan untuk menghasilkan fritz kaca. Fritz kaca itu dikisar dengan halus dan ditapis menjadi bentuk serbuk dengan saiz 63 μm. Ketumpatan kaca SLS-ZnO meningkat dengan peningkatan kepekatan Pr. Sistem kaca yang terdiri daripada fasa amorfus dan lebih banyak oksigen bukan penyambungan (NBO) telah disahkan oleh analisisa XRD dan FTIR. Jurang band turun naik apabila kepekatan Pr lebih rendah daripada 3 wt.% dan dipertingkatkan pada kepekatan Pr yang lebih tinggi (4 dan 5 wt.%). Walau bagaimanapun, keamatan keperdakilauan menurun apabila kepekatan Pr meningkat dari 4 wt.% hingga 5 wt.% mungkin disebabkan oleh kesan kepekatan pelindapkejutan.

Selain itu, seramik kaca Zn_2SiO_4 telah disediakan melalui pensinteran SLS-ZnO kaca dari 600 hingga 1000 ^oC. Pencirian penambahan Pr di dalam Zn_2SiO_4 sampel dinilai dari segi struktur, optik dan kependarkilauan pada suhu pensinteran yang berbeza. Pembentukan α-Zn_2SiO_4 dalam matriks SLS- ZnO dibuktikan oleh analisisa XRD, FTIR, FESEM dan EDX. XRD menunjukkan bahawa puncak keamatan α-Zn_2SiO_4 meningkat dengan peningkatan suhu pensinteran. Keamatan fasa α-Zn_2SiO_4 meningkat dengan meningkatkan kepekatan Pr dari 0 hingga 2 wt.% Pr. Walau

bagaimanapun, keamatan fasa α-Zn_2SiO_4 telah menurun pada 3 wt.% Pr dan meningkat pada kepekatan Pr tertinggi (4 dan 5 wt.% Pr). Spektrum FTIR menunjukkan kehadiran fasa Zn_2SiO_4 dalam rangkaian seramik kaca berlaku pada ~467 dan ~697 cm^{-1} yang disokong oleh analisisa EDX. Mikrograf FESEM menunjukkan pertumbuhan butiran meningkat dengan peningkatan suhu pensinteran. Purata pertumbuhan butiran menurun apabila kepekatan Pr meningkat dari 1 hingga 5 wt.%. Ketajaman jalur penyerapan pada ~444 nm telah meningkat apabila kepekatan Pr dan suhu pensinteran meningkat yang dipersetujui dengan pengujaan LED biru untuk fabrikasi Diode Pemancar Cahaya Putih (WLED).

Jurang jalur meningkat dengan peningkatan suhu pensinteran hingga 900 ^oC dan berkurang dengan pensinteran lebih lanjut pada 1000 ^oC disebabkan oleh kekristalan fasa Zn_2SiO_4. Penggantian penambahan Pr ke dalam matriks tuan rumah akan turun naik dalam jurang jalur apabila kepekatan Pr lebih rendah daripada 4 wt.% dan berkurangan pada 5 wt.% Pr. Peningkatan kekristalan Zn_2SiO_4 disarankan untuk mempertingkatkan kependarkilauan dengan peningkatan suhu pensinteran. Adalah menarik untuk diperhatikan bahawa keamatan keperdakilauan berkurang dengan peningkatan kepekatan Pr hingga 3 wt.% dan kemudian mula meningkat pada 4 dan 5 wt.% Pr disebabkan oleh penggabungan ion Pr^{3+} dalam Zn_2SiO_4. Ini menunjukkan bahawa penambahan Pr di dalam Zn_2SiO_4 mempunyai sifat struktur, optik dan kependarkilauan yang sesuai dan boleh menjadi bahan seramik kaca yang menjanjikan untuk peranti optoelektronik.

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

Jumiah Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Khamirul Amin Matori, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Raba'ah Syahidah Azis, PhD
Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

____
ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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LIST OF ABBREVIATIONS AND SYMBOLS

Zn_2SiO_4	Willemite
ZnO	Zinc Oxide
SiO_2	Silica Oxide
SLS	Soda Lime Silica
α	Alpha
β	Beta/ Constant
ϒ	Gama
Pr_6O_{11}	Praseodymium Oxide
WLEDs	White Light Emitting Diodes
LED	Light Emitting Diodes
Pr^{3+}	Trivalent Praseodymium
Wt.	Weight
T_g	Glass transition
T_c	Temperature Crystallization
XRD	X-ray Diffraction
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Radiation
FESEM	Field Emission Scanning Microscopy
UV-Vis	Ultraviolet-Visible spectrometers
EDX or EDS	Energy Dispersive X-ray Spectroscopy
PL	Photoluminescence
E_u	Urbach energy
h	Plank constant
v	Phonon frequency
$\alpha(v)$	Absorption coefficient
hν	Photon energy
λ	Wavelength
k	Extinction coefficient.
E_g	Optical band gap

CHAPTER 1

INTRODUCTION

1.1 Background of study

In recent years, special attention has been paid to the development of willemite (Zn_2SiO_4) for optical applications because of its unique properties, wide band gap (5.5 ev) and excellent chemical stability. Willemite was first discovered in 1829 in a “calamine” orebody in Belgium by Armand Le´vy in Moresne (Simonov et al., 1977). According to Takesue et al. (2009), the name of willemite was dedicated to King Willem of the Netherlands. Since then, the existence of willemite was found to be distributed all over the world.

Furthermore, Zn_2SiO_4 which formed the binary ZnO-SiO_2 phase system have also been employed extensively as host matrices of rare earth ions for applications in the area of luminescent materials. Hence, the increasing demand in this field has motivated researchers to develop novel inorganic Zn_2SiO_4 phosphor which used a low energy process that would help to solve both energy and environmental problems of our society. There are various methods to synthesize Zn_2SiO_4 such as solid state, sol-gel, hydohermal, solvothermal, co-precipitation, and spray pyrolysis method (Yang et al., 2013). Conventional solid- state method is important for fabrication of willemite due to its long history of practical use. This method involves the sintering and crystallisation of glass samples. Takesue et al. (2009) reported that the raw materials are well mixed and sintered at temperatures between 900 and 1500 ^oC for several hours in an electric furnace to form Zn_2SiO_4 inorganic phosphor. In brief, this method employed here involved the solid diffusion of atoms or atomic groups among solid raw materials. Solid-state methods provide irregularly shaped particles giving particle diameters of the order of microns with a wide size distribution. It was reported by Tammann and Kalsing (1925) that ZnO and SiO_2 react at around 775 ^oC to form Zn_2SiO_4 that is confirmed by the appearance of an exothermic peak with differential scanning calorimetry. The phases of Zn_2SiO_4 are produced by solid-diffusion of ZnO from the surface of SiO_2 are illustrated by the following equation (Leverenz and Urbach, 1950)

$$SiO_2 + 2ZnO = Zn_2SiO_4 \qquad (2.1)$$

Synthesis of Zn_2SiO_4 by sol- gel have had the lowest processing temperatures of all growth methods and produce spherical particles. Usually, this method involved a solvent, such as water, alcohol, ionic liquid and their mixtures at temperatures lower than the boiling point and at ambient pressure. Various Zn and dopant sources (e.g. nitrate, sulfate, chloride, acetate) and Si sources (e.g. silica, silicates, alkoxysilanes, water glass) are used as the starting materials. These materials are dissolved or dispersed in solvents and then mixed to produce a homogenous solution or uniform dispersion. The solutions or dispersions obtained are coated onto a substrate or simply dried. The phase formation of Zn_2SiO_4 by sol gel needs calcinations higher than 800

^{o}C to form α-phase Zn_2SiO_4 (Takesue et al., 2009). Similarly of solid-state method, the sol gel method also involves in high temperatures and based on the diffusion in the solid state in order to produce α-phase Zn_2SiO_4.

The other methods such as hydrothermal and solvothermal can produce α-phase Zn_2SiO_4 without post calcinations. It is indicated that, the crystallization of α-phase Zn_2SiO_4 in solvent occurs at lower temperature than those required in solid diffusion. Generally, hydrothermal methods use water or an aqueous mixture as the reaction medium, while solvothermal methods use organic solvents. The method of hydrothermal and solvothermal are carried out in a Teflon-lined autoclave in which raw materials are loaded and then sintered at temperatures of 100 to 370 ^{o}C. However, this method produced a low crystallinity of Zn_2SiO_4 that have lower luminescence properties compared to the solid-state method.

In this study, the techniques of melt-quenching and solid state were used to produce Zn_2SiO_4 since it has many advantages such as simple process and large-scale production in the industrial operation than the chemical method. Soda Lime Silica (SLS) has been the focus of numerous investigations because of its potential for low temperature viscous flow sintering and promising as low cost integrated optical amplifier. Host matrix based on ZnO has attracted increasing interest because of its wide band gap and large exciting binding energy (60 mev) for application in optoelectronic devices. According to Qian et al. (2008), ZnO act as a network former that is connected to the neighboring SiO_4 to produce Si-O-Zn bond by bridging oxygen. Therefore, the combination of both SLS-ZnO is a promising host matrix for production of Zn_2SiO_4 phosphors due to their low melting point, good stability for rare earth ions and excellent properties in chemical stability and luminescence.

1.2 Phase formation of willemite

Recently, willemite ceramics were widely studied as luminescent material for their high stability and high efficiency. Therefore, the study of crystalline phases of Zn_2SiO_4 ceramics is very important in order to develop useful glass ceramics in optical field.

As shown in Figure 1.1, the melting temperature of Zn_2SiO_4 was 1498 ^{o}C instead of 1512^{o}C as reported by Williamson and Glasser (1964). It forms a eutectic with tridymite at 1,432° C and 49.1 per cent ZnO. Eutectic with ZnO occurred at 1,507° C. and 77.5 mol per cent ZnO. According to the ZnO-SiO_2 binary phase diagram , α phase Zn_2SiO_4 was found in the 51.6 mol per cent ZnO, quenched at 1,440° C, and 65.0 mol per cent ZnO, quenched at 1,505° C. It is known, α phase Zn_2SiO_4 is the stable compound that can be synthesized at temperature greater than approximately 800 ^{o}C and at pressure greater than approximately 3 GPa (Syono et al., 1971). However, there are two metastable phase β-Zn_2SiO_4 and ϒ- Zn_2SiO_4 were reported in Williamson's study. β -Zn_2SiO_4 occurs in rapid cooling of liquid melt with composition between 33.3 and 63 mol% SiO_2, while ϒ- Zn_2SiO_4 is produced by rapid quenching in the compositional range of 45 to 55 mol% SiO_2.

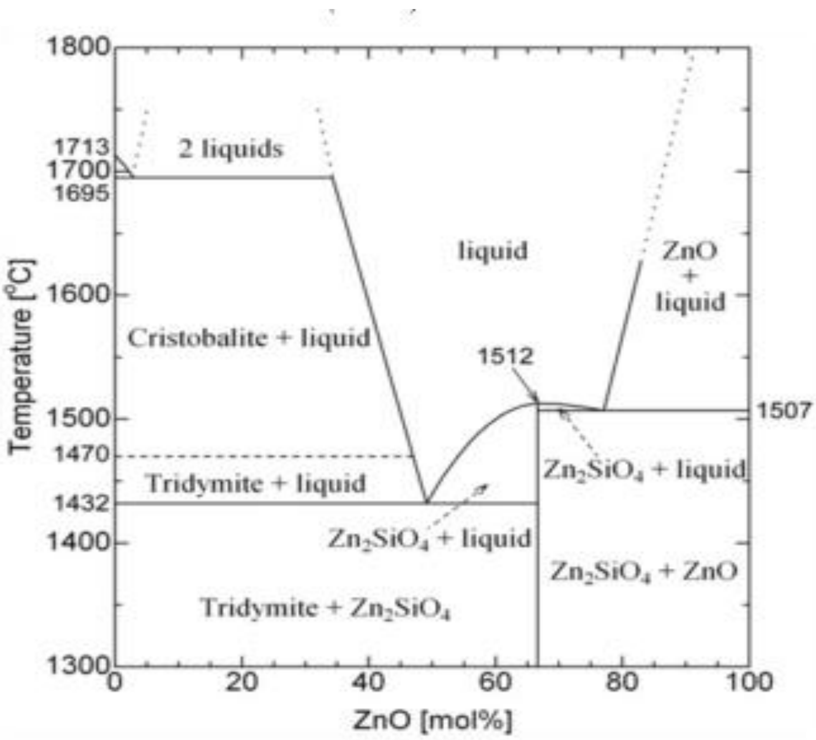

Figure 1.1: Equilibrium phase diagram for ZnO-SiO_2 system (Bunting, 1930)

Figure 1.2 shows α phase Zn_2SiO_4 is a neosilicate or orthosilicates that consist of isolated SiO_4^{4-} tetrahedrons and ZnO_4^{6-} in the zinc silica system. It was reported by Taylor (1962), that ZnO and SiO_2 react at around 775° C to form β-Zn_2SiO_4 which is confirmed by the appearance of an exothermic peak with differential scanning calorimetry. The transformation of orthorhombic - β phase into α -phase appeared at 835°C as an exothermic reaction according to thermal analysis methods Gotz and Masson (1978)

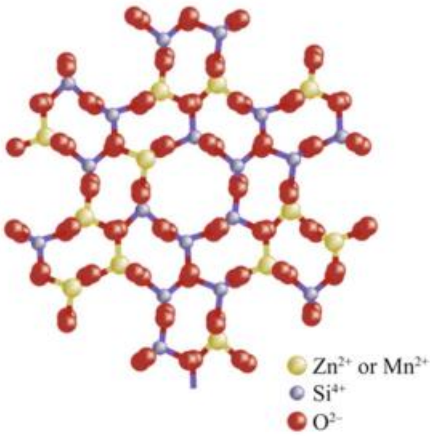

Figure 1.2: Crystalline structure of α phase Zn_2SiO_4 (Lukic et al., 2008)

1.3 Significant and motivation of research

White Light Emitting Diodes (WLEDs) are of interest in optoelectronics field because of their benefits in terms of long lifetime, long energy consumption, high luminous efficiency and reliability. Generally, the most common technique to produce WLEDs by coating yellow phosphor on the surface GaN blue LED chips. However, they have low color rendering index due to lack of red content. Among rare earth materials, trivalent Praseodymium (Pr^{3+}) ions are considered as a promising red activator in host materials via red emission wavelengths at ~618 nm and ~650nm. Besides Pr^{3+} ions having strong blue excitation in the wavelength at ~450 nm. It is significant to search for a stable red phosphor with environmental friendliness under blue excitation for WLEDs application. Thus, this study has been focused on structural, luminescence and optical properties of Pr doped SLS-ZnO glass ceramics at varying sintering temperature for the production of low cost red Zn_2SiO_4 phosphors.

1.4 Problem statements

Nowadays, the combination of SiO_2-ZnO are of great interest as a host lattice for the fabrication of efficient optical system. However, pure SiO_2 glasses with high viscosity requires melting temperature at above 2000 ^oC may lead to high cost for mass production. Thus, SLS glasses are potential candidates for synthesizing SiO_2 would be an effective effort in reducing disposal cost and preserving environment. According to Chimalawong et al. (2010), SiO_2 glass is a suitable host matrix for rare earth ions due to its interesting properties such as good durability, good chemical stability and high UV transparency.

The production of Zn_2SiO_4 glass ceramics by utilizing SLS-ZnO glass may lead to high homogeneity, well controlled dopant concentration, easy fabrication and improved optical properties. From previous literatures (Gao, 2013), rare earth ions incorporated into glass ceramics enhanced PL properties by changing of ligand field around rare earth ions. Regarding to the enhancement of PL properties, Pr^{3+} is a very interesting rare earth ion which offers the possibility of simultaneous emission wavelength in the blue, green, orange, red and infrared region. However, there is limited report on Pr doped Zn_2SiO_4 glass ceramics system for optical and PL properties. Therefore, the knowledge of structural, thermal, optical and luminescence properties is a very useful tool in order to develop a new kind of Pr doped Zn_2SiO_4 glass ceramics for optoelectronic application.

1.5 Objectives

1.5.1 Main research project objective

The main objective of this research project is to produce a low cost red emitting phosphor glass ceramic with strong absorption in the blue wavelength region. Generally, phosphor host material is based on Zn_2SiO_4 can be identified as a proper host material which achieves excellent luminescence. Trivalent Praseodymium (Pr^{3+}) ions doped into Zn_2SiO_4 matrix are interesting due to search for new material in the field of optoelectronic devices. Therefore, it is necessary to develop a red Zn_2SiO_4 phosphor based on SLS– ZnO host matrix doped with Pr without incorporating expensive materials.

1.5.2 Work-phase objectives

Hence, this research embarks on the following work-phase objectives which are:

1. To synthesize Zn_2SiO_4 based glass ceramics added with Pr_6O_{11} by conventional melt-quenching method.
2. To investigate the effect of Pr addition on structural, optical and luminescence properties of Zn_2SiO_4 at different sintering temperatures.
3. To study the effect of Pr^{3+} addition in Zn_2SiO_4 on phase formation and microstructure at different sintering temperatures.

1.6 Hypothesis

According to work phase objectives, this study is hypothesized as follows;

1. The glass transition would increase with increase of Pr content due to the formation of non-bridging oxygen in SLS-ZnO glass matrix, thus increasing the optical and luminescence properties.
2. The crystalline peaks of Pr addition in Zn_2SiO_4 would increase with increase in sintering temperature. It is expected that, Pr^{3+} would incorporate into the Zn_2SiO_4 host matrix in a successful substitution of Zn^{2+} by Pr^{3+} in the Zn_2SiO_4 framework.
3. Optical and luminescence properties of Pr addition in Zn_2SiO_4 would enhance with increase in sintering temperature. The introduction of Pr into Zn_2SiO_4 would achieve red emission intensity for the red phosphor.

1.7 Thesis outline

The thesis is organised according to the following chapters. The general introduction of willemite, its phase formation and a statement of the motivation, problems as well as objectives and hypothesis of the research are provided in Chapter 1. In Chapter 2, the framework of research area is presented by literature surveys on density, thermal, structural, optical and luminescence properties of willemite materials. Chapter 3 describes the related theories on optical absorption and luminescence of glass and glass ceramics systems. The details of the experimental techniques employed in this research are discussed in Chapter 4. The results of the Pr addition willemite glass ceramics materials at different sintering temperatures are presented in Chapter 5. Chapter 6 summarizes the results as conclusion and suggestions for future work in Pr addition willemite system.

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