THE SYNTHESIS OF NON-STOICHIOMETRIC CORDIERITE VIA GLASS CERAMIC ROUTE USING CALCINED TALC AND KAOLIN

by

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LIST OF ABBREVIATIONS

IC	-	Integrated circuit
DTA	-	Differential Thermal Analyses
XRF	-	X-ray florescence
XRD	-	X-ray diffraction
FEG	-	Field emission gun
BSE	-	Backscattered electron
SEI	-	Secondary electron Image
PSD	-	Particle size distribution
HELOS	-	Helium neon optical system
CTE	-	Coefficient of thermal expansion
MAS	-	Magnesium aluminum silicate
APS	-	Amorphous phase separation
ICSD	-	Inorganic Crystal Structure Data
ICDD	-	Inorganic Crystalline Diffraction Data
PDF	-	Powder diffraction file
TEOS	-	Tetraethylorthosilicate
SRM	-	Standard reference material
NIST	-	National institute of standard technologist
RIR	-	Reference intensity ratio
wt%	-	Weight percent
kJ	-	Kilo joule
rpm	-	Rotation per minute
μm	-	Micron meter
MPa	-	Mega Pascal

LIST OF SYMBOLS

α'	:	Total polarization
α_e	:	Electronic polarization
α_i	:	Ionic polarization
α_o	:	Orientation polarization
α_f	:	Interfacial polarization
α''	:	Polarizability of each molecule
σ'	:	Thermal stress
σ_i	:	Interfacial energy
α_l	:	Linear thermal expansion
α_a	:	CTE at lattice *a* direction
Δ	:	Distortion index
D	:	Diffusion coefficient
d	:	Inter planar spacing
E	:	Elastic modulus
ε	:	Relative dielectric constant
ε''	:	Loss factor
ε_o	:	Permittivity of free space
I_o	:	Nucleation rate
U	:	Crystal growth rate
ΔG	:	Gibbs free energy
ΔG_D	:	Diffusion rate
η	:	Viscosity coefficient
H	:	Entalphy
ρ	:	Density
ΔE	:	Energy barrier or activation energy
a	:	Inter atomic spacing
v	:	Atomic jump frequency
c	:	Constant
c'	:	Concentration
σ	:	Conductivity
F	:	Frequency

F_o	:	Resonance frequency
γ	:	Surface tension
I_o	:	Observed diffraction line
I_c	:	Calculated diffraction line
l_i	:	Initial length at room temperature
l_f	:	Length at final te,mperature
J	:	Flux
k	:	Dielectric constant
M_e	:	Mass of electron
M	:	Metal species
m	:	Slope in Arrhenius plot
η	:	Wavelength
n	:	Integer
OR	:	Alkoxyl group
P_n	:	Pressure at n area
Q	:	Activation energy for densification
Θ	:	Thetha
R	:	Gas constant
R_{Bragg}	:	Agreement indice on Bragg value
R_{wp}	:	Agreement indices on weighted value
R_{exp}	:	Agreement indiced on expected value
R_p	:	Agreement indices on profile value
r*	:	Critical radius
S	:	Entrophy
s	:	Goodness of fit
T_g	:	Glass transition temperature
t_n	:	Minimum quenching time to avoid crystallization
Tan α	:	Dissipation factor
T_p	:	Crystallization temperature at peak in exothermal DTA curve
T_i	:	Initial temperature
T_f	:	Final temperature
T_m	:	Melting temperature
V	:	Volume

V_i	:	Volume fraction of each phase
ν	:	Poisson ratio
W*	:	Thermodynamic barrier
W_d	:	Weight of dry pellet
W_s	:	Weight of suspended pellet
W_w	:	Weight of saturated pellet
X_c	:	Crystallization mass fraction
X_a	:	Non-crystallized mass fraction
x	:	Direction of diffusion
Z	:	Number of electron per atom

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SINTESIS KORDIRIT TAK STOIKIOMETRIK MELALUI KAEDAH KACA-SERAMIK MENGGUNAKAN TALKUM DAN KAOLIN TERKALSIN

ABSTRAK

Pelbagai komposisi tak stoikiometrik kordirit telah disintesis melalui kaedah penghabluran kaca. Kelakuan pemadatan dan penghabluran kaca ditentukan menggunakan ujian dilatometri, dan analisis pembezaan terma. Manakala transformasi fasa kaca ke kaca-seramik menggunakan pembelauan sinar-x. ujian pekali pengembangan terma, sifat dielektik, ketumpatan dan peratus porositi serta mikrostruktur kaca-seramik dilakukan untuk mengaitkan perubahannya terhadap komposisi. 100 wt% fasa hablur α-kordierit dengan ketumpatan 2.54 g/cm^3, porositi 0.4 % telah berjaya diperolehi pada suhu rawatan haba serendah 900^{o}C selama 2 jam menggunakan komposisi tak stoikiometrik kordirit yang di sintesis menggunakan talkum dan kaolin terkalsin sebagai bahan mula. Ini menunjukkan komposisi ini sesuai untuk aplikasi LTCC. Pekali pengembangan terma (2 x 10^{-6} C^{-1}), pemalar dielektrik (5.5) and kehilangan dielektrik (1.6 x 10^{-2}) yang diperolehi juga memenuhi sifat-sifat yang diperlukan untuk aplikasi frekuasi tinggi. Fasa separuh amorfus pada serbuk kaca mula perlu dielakkan kerana ia akan memberikan kesan yang besar pada kelakuan pemadatan dan penghabluran kaca. α-kordierit yang di sintesis dari mineral sebagai bahan mula mempunyai sifat-sifat yang standing dengan α-kordirit yang dihasilkan dari oksida tulen. Namun, ia mempunyai darjah penghabluran yang rendah dan mempunyai kehilangan dielektik yang tinggi berbanding sampel yang disintesis menggunakan oksida tulen. Penambahan B_2O_3 and P_2O_5 sangat berkesan dalam menurunkan suhu pelembutan tetapi tidak semestinya meningkatkan proses penghabluran. Ia hanya berkesan pada sampel-sampel dalam siri $xMgO.2Al_2O_3.5SiO_2$ yang mempunyai bilangan mol MgO yang rendah. Adalah sangat penting untuk melebur campuran komponen di atas suhu peleburan sebelum penghabluran kerana sistem kaca + kaca-seramik dalam system yang sama tidak dapat meningkatkan pemadatan disebabkan oleh halangan kinetik yang tinggi di antara sistem.

THE SYNTHESIS OF NON-STOICHIOMETRIC CORDIERITE VIA GLASS CERAMIC ROUTE USING CALCINED TALC AND KAOLIN

ABSTRACT

Various non-stoichiometric cordierite compositions were synthesized via glass route. Densification and crystallization behavior of the glass were determined by dilatometry and differential thermal analysis, while phase transformation of glass to glass-ceramic by X-ray diffraction. CTE, dielectric properties, density and porosity percentages as well as the microstructure of glass-ceramic were carried out to correlate its variation with the compositions. 100 wt% α-cordierite phase with the density 2.54 g/cm^3, porosity 0.4% has succesfully being obtained at lower heat treatment temperature of 900^{o}C for 2 hours using non-stoichiometric cordierite compositions synthesized from mainly calcined talc and kaolin as initial raw materials. This demonstrates that this composition is suitable for LTCC application. The CTE (2 x 10^{-6} C^{-1}), dielectric constant (5.5) and dielectric loss (1.6 x 10^{-2}) obtained are also fulfilled the properties required for high frequency application. Partially amorphous phase in initial glass powder should be avoided since it will significantly affect the densification and crystallization behavior of the glass. α-cordierite synthesized from minerals as raw materials has a comparable properties with the one synthesized reagent grade oxide. Although it has slightly lower degree of crystallinity and high dielectric loss, however it has lower densification and crystallization temperature as compared to composition synthesized from the reagent grade oxides. The addition B_2O_3 and P_2O_5 are effective in reducing the softening temperature but not necessarily enhance the crystallization process. The addition of B_2O_3 and P_2O_5 is only effective for samples in the series $xMgO.2Al_2O_3.5SiO_2$ with lower MgO mole. It is also a very important to melt the mixtures of compounds above its melting point before crystallize since glass plus glass-ceramic in the same system would not facilitate densification due to its relatively high kinetic barrier within the system.

CHAPTER 1
INTRODUCTION

1.1 Introduction

Recently, high circuit density packages for miniaturization and for lightweight integrated electronic assembly are required in wireless communication and high frequency applications [1, 2]. Therefore, several researches on compact multilayer structures with buried passive components has gain an interest among the reseachers [3, 4]. The use of multilayer substrate decreased the time it takes for the signal to be transmitted. Hence, material with low dielectric constant is required by semiconductor industry to meet the challenge of improving integrated circuit speed by reducing the capacitance and crosstalk between metal-to-metal interconnections [5]. In addition, the thermal coefficient of the materials should also be closely matched with the chips material which is usually silicon. If the expansions were not closely matched, then the reliability of the package is reduced. If the mismatch is large enough, there will be stresses on the solder part and between the chip and the substrate. These can lead to cracking of the pads and results in open circuit and chip detachment from the substrate, which finally leads to a catastrophic failure.

Many researches have been done on multilayer structure e.g. low temperature cofired ceramic, LTCC materials and among them that have been proposed as one of the most suitable materials is cordierite since it has low dielectric constant (ε = 5–6), high resistivity ($\rho > 10^{12}$ Ωcm), elevated thermal and chemical stabilities, very low coefficient of thermal expansion, CTE (α=1–2 x 10^{-6} C^{-1}), and excellent insulation properties [6]. These are the properties of high purity and crystallinity of α-cordierite

phase which normally can be obtained by sintering cordierite initial powders at temperature above 1200°C [7-9]. Although α-cordierite is a promising material for high speed application due to its low dielectric constant, low dissipation factor and low thermal expansion, but it is difficult to crystallize and sinter α-cordierite phase below 1000°C because of its sintering temperature range (1200-1350^{o}C) [10-13] is near to the incongruent melting point of the cordierite. It has the incongruent melting point because the solid compound of cordierite does not melt to form the liquid of its composition , but instead dissociates to form a new solid phase and the liquid. The lowest liquidus temperature is at the tridymite-protoenstatite-cordierite eutectic at 1345^{o}C, and cordierite-enstatite-forsterite at 1360^{o}C [14]. Many researches have been conducted in order to find out how to decrease the sintering temperature of cordierite. Some of them have used flux or additives whilst others have tried to synthesize it using different method such as sol-gel process, non hydrolytic sol-gel process and cordierite glass powder. Among those techniques, glass-ceramic route has successfully obtained α-cordierite at and below 1000°C [15-21]. IThe sintering temperature of the dielectric materials has to be reduced $\leq$ 900^{o}C [22, 23] in order to allow metal pastes with high electrical conductivity e.g. Ag, Au, and Cu. This is because of the sintering temperature of Ag, Au or Cu electrodes (the melting point of Ag: 961.93^{o}C, Au: 1064.43 ^{o}C, Cu: 1083^{o}C) in multilayer device has limit the sintering temperature of the substrate to 0.7 of its melting point (0.7T_m). Therefore, all glass powders with various compositions in the present study were characterized after subjected to 900^{o}C heat treatment temperature.

It is not enough to crystallize α-cordierite below 1000^{o}C by only applying crystallization of glass method. Normally various nucleating agent or sintering aids were also used. Although some of these authors have successfully crystallized α-cordierite to below 1000^{o}C by the addition of additives, however other secondary phases were also present and as a result it will degrade some of the required properties. By using cordierite composition with additives, Chen et al. [21] and Wang et al. [18] had successfully synthesized α-cordierite below 1000°C. However, Chen et al. [20, 21] found that although the increasing of CaO or ZnO content could decrease the crystallization temperature of α-cordierite and increased the peak intensity of α-cordierite but other phase which are gahnite and mullite [20] are also present which finally increase the coefficient of thermal expansionn CTE of samples. Wang et al. had used less than 5 wt %, B_2O_3 and P_2O_5 and only small amount of α-cordierite was found to crystallize at 850°C, and a single phase of α-cordierite was only obtained at 1050°C [18].

In magnesium aluminum silicate (MAS) glass system, MgO is a modifying oxide, Al_2O_3 is an intermediate oxide and SiO_2 is a glass former [24]. Modification on the ratio of MAS system would be beneficial to lower the viscosity of the glass and enhance the nucleation rate. It was reported in the literature reviews [20, 21, 25-27] using pure oxide as initial raw materials that cordierite composition with excess MgO and less Al_2O_3 would also contribute to better densification and crystallization behavior. Since an excess of MgO from stoichiometric cordierite composition could retard the formation of μ-cordierite, enhanced the densification and crystallization

behavior of α-cordierite phase, a few series of non-stoichiometric cordierite compositions were studied in the initial stage without any additives using mainly talc and kaolin, and crystallization by the glass route has been selected as method of synthesis.

There were various types and mixtures of raw materials have been used to synthesize α-cordierite. Talc and kaolin which contain high amount of MgO, Al_2O_3 and SiO_2 have also been used as the initial raw materials for synthesing α-cordierite. Even though, there are many studies on the synthesized of α-cordierite using talc and kaolin as the starting raw materials together with other minerals such as magnesium compounds [39], silica, alumina [40], gibbsite [31,41], calcined alumina and fly ash [32], magnesium oxide [42], diatomite and alumina [36], silica, sepiolite and feldspar [43], fly ash, fused silica and alumina mixture [33], alumina [44,45]; however, most of them followedg solid state reaction route except two [1,10] used glass crystallization method. The presence of secondary phases on sintered samples previously reported using these minerals, together with the existence ofimpurities content in the minerals may be the reasons of limited researches found on crystallization of α-cordierite from minerals by glass-ceramic route especially for electronic packaging application. Conversely, talc and kaolin contain alkali oxides and alkaline earth oxides which may facilitate in decreasing the melting temperature as well as its densification and crystallization temperature of glass-ceramic.

For that reason, in this present study talc and kaolin were selected as the main initial raw materials for synthesizing α-cordierite, while small amount of MgO,

Al_2O_3, SiO_2 were added just to compensate the chemical formulation. Comprehensive investigation on the glass-ceramic between two groups of samples from different initial raw materials namely pure oxides and minerals with the same $MgO:Al_2O_3:SiO_2$ (MAS) ratios and similar processing parameters is essential to provide an understanding on how the impurities affect the properties of glass-ceramic. Therefore, a few samples of the same formulations were produced from pure oxide for detail observation on the trend of phase transition, densification and crystallization of samples and then, make a comprehensive comparison with samples produced using mainly talc and kaolin as initial raw materials.

The combination of P_2O_5 and B_2O_3 are commonly used in crystallization of α-cordierite from glass [18, 21, 28-33]. Although the addition of B_2O_3 and P_2O_5 is effective to enhance the densification and crystallization of α-cordierite phase, however, the final glass-ceramic properties would deteriorate if too much nucleating agent were added in the compositions. Therefore, the effect of the addition of 3 wt% B_2O_3 and 2 wt% P_2O_5 in selected non-stoichiometric samples were examined in the present study.

Apart from that, others parameters could also affect the final properties of cordierite. Hing et al. [34] studied on the effect of processing parameters on the sinterability, microstructures and dielectric properties of glass ceramics in the cordierite phase field. They found that the nature of the precursors have a very marked effect on the densification, microstructures and dielectric properties of the sintered components. For example, mechanical milling caused surface area,

activation energy, and particle size of the initial raw materials to change. Many atoms and ion are at the surface with finer particles, and as a results, a collection of fine particles of a certain mass has higher energy than for a solid cohesive material of the same mass [35]. High surface area and accumulated energy produced has caused the reaction between particles easily occured at much lower temperature during solid state reaction.. The changes in surface area, particle size and distribution of particle size have a direct influence on the final properties. This is because final properties of end product depend on structure, mass transport and reactivity. A study had proven that the sintering temperature of certain materials could be lowered by a modification of particle size, its distribution and degree of crystallinity. Even though the chemical compositions of the mixture are the same, but the accumulated energy produced during mechanical activation give significant effect on phase transformation during sintering. It was proven that mechanical milling can caused the loss of crystalline structure of the initial powder and the increase in reactivity [36]. Yalamac et al. [37] who have conducted research on intensive grinding effect on cordierite synthesis by solid state reaction using kaolin, talc and $Al(OH)_3$ as precursor found that, by mechanical activation (maximum speed 500 rpm and maximum milling time 60 min) cordierite can be crystallized at 1100°C instead of above 1200^{o}C [7-9] by using solid state reaction process. Furthermore, they found that a combination of additives and mechanical activation of the powder could lower the synthesis temperature of α-cordierite phase at 1000°C. Therefore, frits that were obtained from all compositions were subjected to high energy milling using planetary mill with tungsten carbide as its grinding media. Frits were pulverized to a very fine glass powder with average particles size of 1-3 μm.

In this study α-cordierite sample was prepared in the form of bulk sample. Investigation on phase transformation, densification and crystallization behavior of glass to glass-ceramic is important to determine which compositions could produce dense, high purity and high crystalline of α-cordierite phase at lower crystallization heat treatment temperature (900^{o}C). Therefore, to determine this, dilatometry test of unsintered glass powder, isothermal and non-isothermal DTA, XRD analysis of glass powder and sintered pellet were carried out. Beside the densification and crystallization temperature, the purity and degree of crystallinity of α-cordierite phase will also determine the best selection of composition used for synthesizing α-cordierite phase. Rietveld method was employed for quantitative phase analysis while Full Profile method for measuring the crystallinity of α-cordierite phase. Microstructure of the fractured surface, its density and porosity tests will be used to support the results. Meanwhile the results of CTE and dielectric test would confirm the physical characteristic of the samples in order for it to be used as a material for high frequency applications.

1.2 Problem statement

Single phase or pure α-cordierite with high degree of crystallinity had been produced by previous researchers which is suitable to be used for LTCC or substrate for high frequency application. However that particular α-cordierite was obtained at higher temperature of above 1200°C. In order for it to be used for that application, α-cordierite phase has to be synthesized around 900°C. Only a few researches, have successfully crystallized α-cordierite from glass route below 1000^{o}C after using pure

oxides as precursors with non-stoichiometric cordierite composition together with the addition of sintering aids or nucleating agent. However, small amount of secondary phases were still present. Thus, investigation on non-stoichiometric compositions in MAS system is necessary to obtain high purity and high degree of crystallinity of α-cordierite phase. The use of pure oxide is more costly compared to the use of talc and kaolin as initial raw materials. Furthermore, the minerals used in the present study contain alkali oxides and alkaline earth oxides elements which could act as fluxes. Therefore, with appropriate composition design, there is a possibility to decrease the melting and crystallization temperature using these minerals.

1.3 Research objectives

This study is mainly concentrating on the characterization of various stoichiometric and non-stoichiometric cordierite compositions by crystallization of glass method using mainly talc and kaolin as initial precursors to obtain highest purity and crystalinity of α-cordierite phase at lower sintering temperature (900^{o}C). Therefore, the main objectives are:

i. To synthesize and study on the densification, crystallization and properties of various cordierite phase from mainly talc and kaolin without the addition of sintering aids: a) $xMgO.2Al_2O_3.5SiO_2$, when x = 2.0 to 4, and b) $xMgO.1.5Al_2O_3.5SiO_2$ when x= 2.6 to 3.0.

ii. To investigate the effect of the addition of fixed amount of sintering aids (3 wt% B_2O_3 and 2 wt% P_2O_5) in selected stoichiometric formulations on their densification, crystallization and end properties of crystallized glass.

iii. To compare densification, crystallization and properties of selected stoichiometric cordierite synthesized from pure oxides with the one synthesized using mainly talc and kaolin.

iv. To observe the effect of melting temperature to densification and crystallization of glass and glass-ceramicproduce from mainly talc and kaolin as the raw materials.

1.4 Scope of research

i. In general, this study is divided into 7 Parts. Characterization of material aree carried out in Part 1. Chacterization of glass and glass-ceramic from non-stoichiometric cordierite composition are carried out in Part 2. In this part, the erffect of varying MgO mole from the exact stoichiometric was studied. Based on the results obtained from Part 2, a series of samples with excess MgO and less Al_2O_3 were produced and characterized in Part 3 to further retard the formation of secondary phase. Upon completion of Part 2 and Part 3, a few MAS composition from the above series was selected. The effect of the addition of small and fixed amount of sintering aid was examined in Part 4. The sintering aids were mixed with glass-ceramic precursors in ball milling and were subjected to similar processing parameters as the previous one. In Part 5, selected MAS composition was reproduced using pure oxides as initial raw materials to observe the trend of phase transition, densification and crystallization of glass as a function of MgO mole. The best composition from pure oxides and minerals were selected and a detailed comparison will be reported in Part 6 on whether the

characteristic of α-cordierite synthesized using mainly talc and kaolin could be as good as the one synthesized using pure oxides. In order to further reduce the cost of melting, effect of melting temperature was studied in Part 7.

ii. A study on phase transformation of glass from amorphous phase to crystalline state was studied using X-ray diffraction of fine glass powder. Qualitatitive and quantitative analysis were carried out using HighScore Plus software. Phase content, lattice change, crystallite size, degree of crystallity and crystal structure analysis of samples were revealed by Rietveld method.

iii. A non-isothermal dilatometry test was carried out on green body samples to observe the sintering reaction and shrinkage of sample at elevated temperature. From the shrinkage curve, the softening temperature or temperature at which the densification process obviously started and stopped was estimated. Activation energy for densification was also measured from dilatometry curve using Arrhenius equation.

iv. Crystallization behavior was studied by isothermal and non-isothermal DTA analysis of all glass powder samples to determine temperature range of crystallization. From the dilatometry and DTA analyses, conclusion can be made as to which compositions have low densification and crystallization temperature. Furthermore, temperature difference between the temperature at which densification has almost completed and the temperature at which crystallization started, as well as it's total percentage of shrinkage during sintering will determine the extent of how good the densification of samples.

v. The effect of phase transition, densification and crystallization of glass as a function of variable parameters (compositions, melting temperature, sintering aids) would varies the properties of materials e.g.the CTE and dielectric properties of the sintered samples. Therefore, these properties were measured using dilatometer model Linseis and impedance analyzer (Hewlett Packard model HP4291) in order to identify its changes towards variable parameters, and consequently outline which compositions are close to therequiredd properties for high frequency application (dielectric constant as low as possible (~5), low CTE which is close to Si chips –(3-3.5x10^{-6}/C) [21].

vi. Density, porosity, and the microstructure analyses of sintered pellets were examined to support the discussions on the densification of samples

CHAPTER 2
LITERATURE REVIEW

2.1 α-Cordierite

Indialite, high cordierite or hexagonal cordierite are the terms that are sometime being used to name α-cordierite. The stoichiometric formula of α-cordierite is $2MgO.2Al_2O_3.5SiO_2$. α-cordierite is one of the polymorph in cordierite system. Its density is 2.512 g/cm^3 and has high melting temperature which is 1460^oC) [14].

α-cordierite has been extensively studied due to their excellent properties e.g. low thermal coefficient, low dielectric constant, excellent thermal shock resistance, as well as high chemical and thermal stability. The application and potential of α-cordierite materials cover a wide range of fields such as refractories, electrical, insulator, filters, membranes, heating elements, microwave absorbants, multilayer chip inductor [18], electromagnetic wave absorbants [38], honeycomb catalytic support for automobiles [39, 40] and low temperature cofired ceramic (LTCC) [5, 21, 41] .

2.2 $MgO-Al_2O_3-SiO_2$ phase

In order to understand the crystallization behavior of cordierite precursor on heating, equilibrium phase diagrams of the $MgO-Al_2O_3-SiO_2$ system are needed. All primary phases obtained from these phase diagrams provide useful information to

further predict the secondary phases in the MgO-Al_2O_3-SiO_2 system. Figure 2.1 shows the ternary phase diagram of MgO-Al_2O_3-SiO_2 system. Beside cordierite, other phases such as forsterite, spinel, sapphrine, enstatite, crystobalite, trydimite, mullite, periclase, and corundum may exist in MAS system, and it's greatly depended on the MAS compositions and the sintering temperatures.

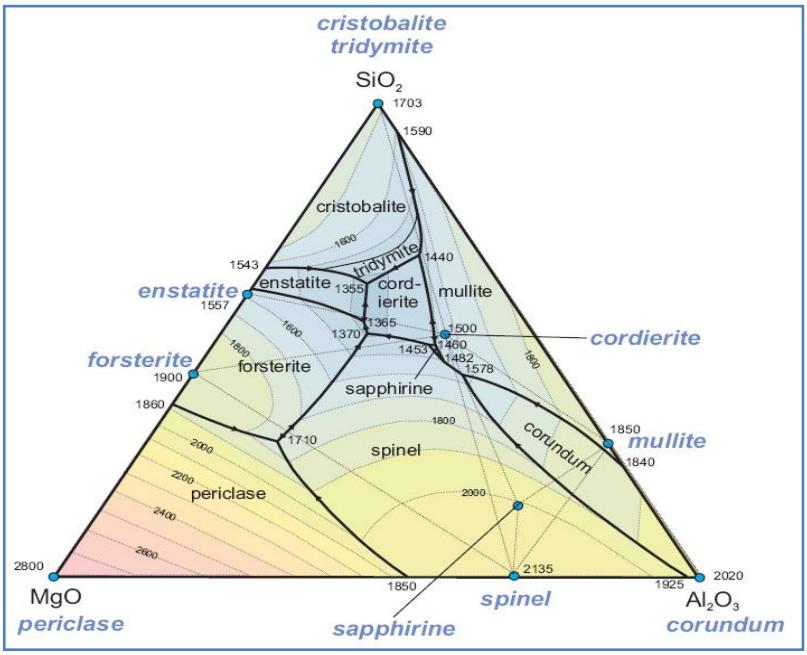

Figure 2.1 Ternary phase diagram of MgO-Al_2O_3-SiO_2 [42]

2.3 Polymorphism of cordierite

Codierite exist under three polymorphic forms: i) hexaganol cordierite, high cordierite, indialite or α-cordierite with a space group P6/mmc, ii) orthorhombic or β-cordierite with a space group Cccm, and iii) meta-stable form referred to μ-cordierite or magnesium aluminum silicate with a space group P6222/160. μ-cordierite is a solid solution with β-quartz structure [43]. Both μ-cordierite and β-

quartz has the same space group with slightly similar diffraction pattern and similar arrangement of atoms in the crystal as shown in Figure 2.2. In μ-cordierite the Mg^{+2} cation occupying octahedral sites between the two tetrahedral sites.

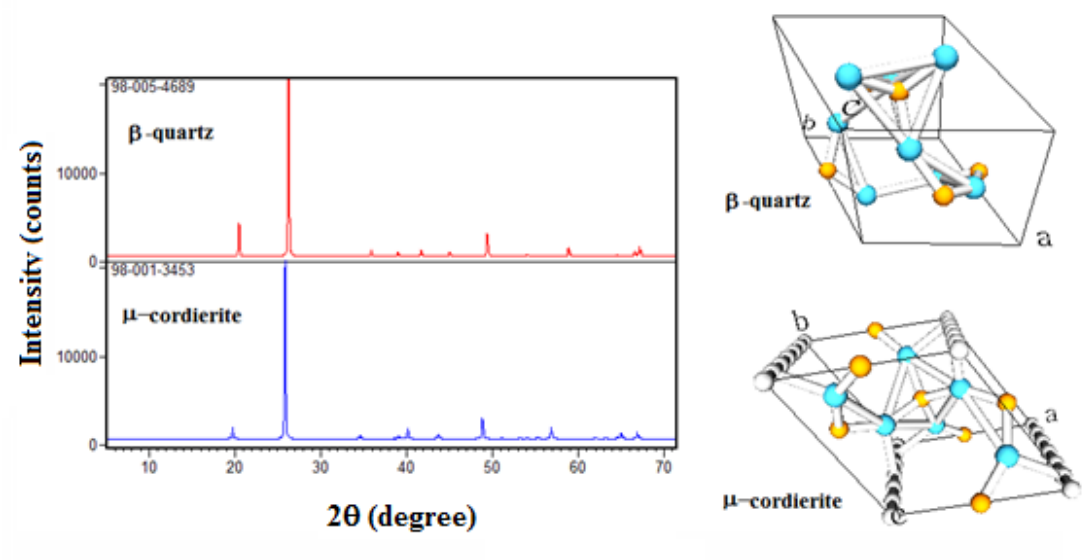

Figure 2.2 Diffraction pattern and crystal structure plots of μ-cordierite and β-quartz

The crystal structure plots for the three polymorphs are shown in Figure 2.3 to Figure 2.5. Table 2.1 shows crystal structure data of the three cordierite polymorphs.

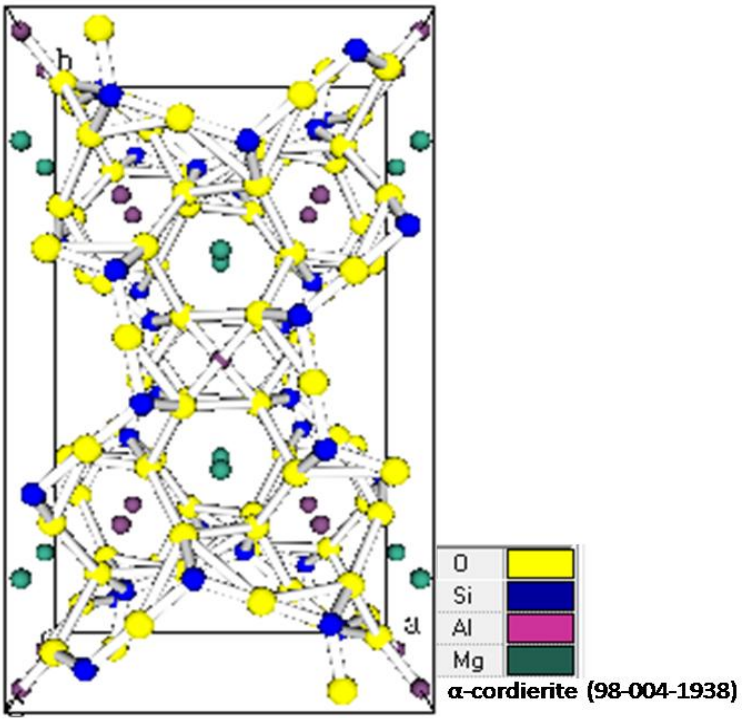

Figure 2.3 Crystal structure of α-cordierite (ICSD 98-004-1938)

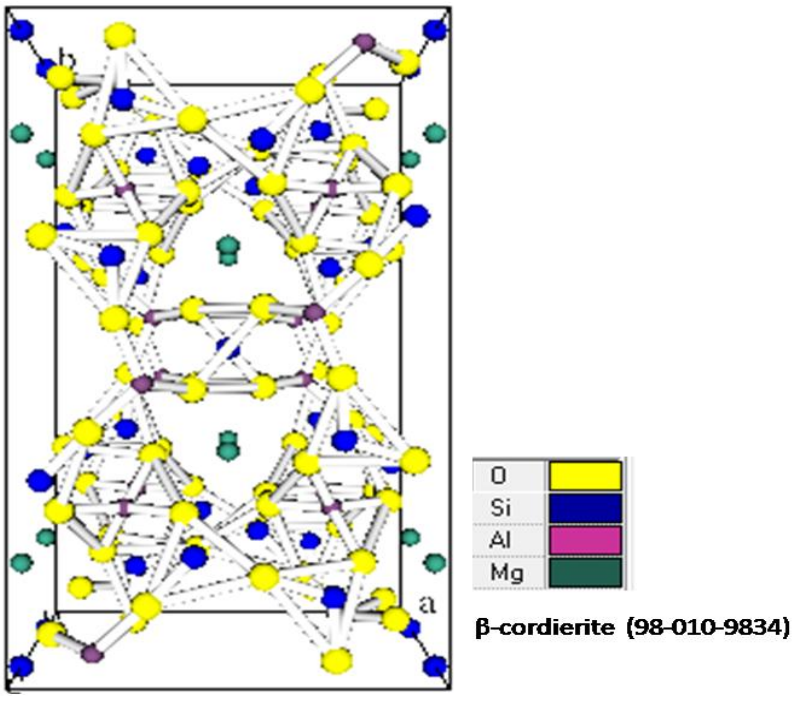

Figure 2.4 Crystal structure of β-cordierite (ICSD 98-010-9834)

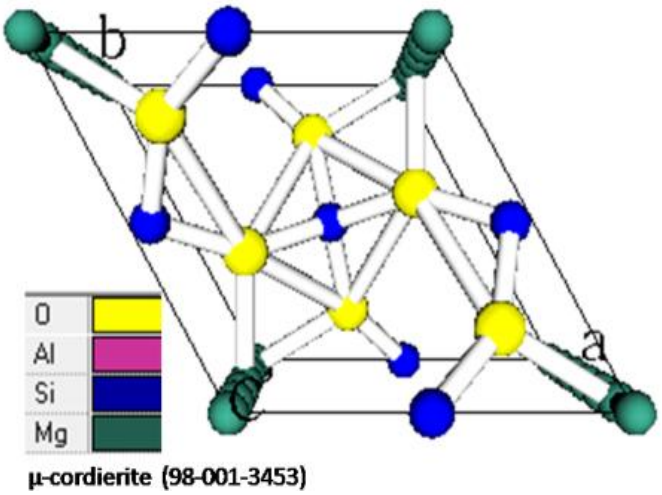

Figure 2.5 Crystal structure of μ-cordierite (ICSD 98-001-3453)

Table 2.1 Crystal data for μ-cordierite, α-cordierite and β-cordierite taken from Inorganic Crystal Structure Database (ICSD)

Property	μ-Cordierite	α-Cordierite or high cordierite	β-Cordierite or low cordierite
Crystal system	Hexagonal (a=b≠c)	Hexagonal (a=b≠c)	Orthorhombic a≠b≠c
ICSD no	98-001-3453	98-004-1938	98-010-9834
Space group	P6222(160)	P6/mcc(192)	Cccm (66)
Lattice *a*	5.182	9.768	9.647
Lattice *b*	5.182	9.768	16.975
Lattice *c*	5.360	9.341	9.2740
Distortion index (Δ)	n/a	0	0.24°

Acording to Velasko et al. cordierite have a tetrahedral silicates framework with the simplified structure formula $Mg_2Al_4Si_5O_{18}$. The Al and Si atoms are distributed over tetrahedral sites (T) which is three T1 and six T2 site performula units [44]. Sai Sundar et al. described the structure of cordierite are built up layers of

corners-shared tetrahedral $(S/Al)O_4$ and octahedral [45]. There are two types of layer. First layers are the layers of $(S/Al)O_4$ tetrahedral forming hexagonal ring, and the second layers with $(S/Al)O_4$ tetrahedral intermixed with MgO_6. The hexagonal and orthorhombic structures are characterized by their six-membered rings of tetrahedrally coordinated cations (T2) which was perpendicular to *c* axis. Mg atoms are located in slightly flattened octahedral. Alternate layers of the hexagonal rings structure are connected through Mg octahedral and T1 tetrahedra. Silicon occupies mostly T2 tetrahedra, and aluminum T1 tetrahedra. The difference between α-cordierites and β-cordierite lies in a greater or lesser degree of disorder between the aluminum and silicon atoms within T1 and T2 sites [43]. The diffraction pattern of β-cordierite and α-cordierite are very similar as shown in Figure 2.6.

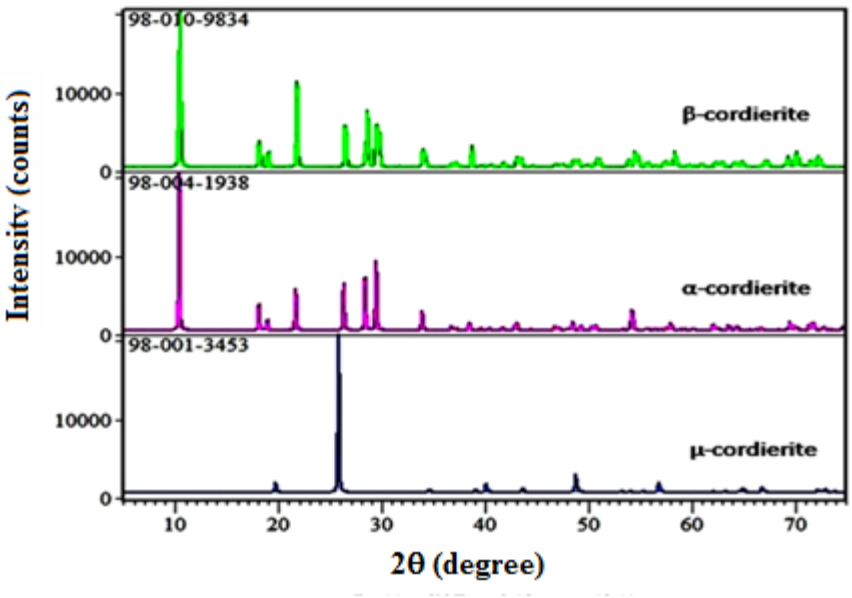

Figure 2.6 Reference pattern of 3 cordierite polymorphs α-cordierite, β-cordierite, μ-cordierite

Both α-cordierite and β-cordierite polymorphs can be distinguished by evaluating the 2θ range from 28° to 30° as shown in Figure 2.7. In this range, one can see that α-cordierite displays only 2 peaks, while cordierite displays up to 5 different peaks [44].

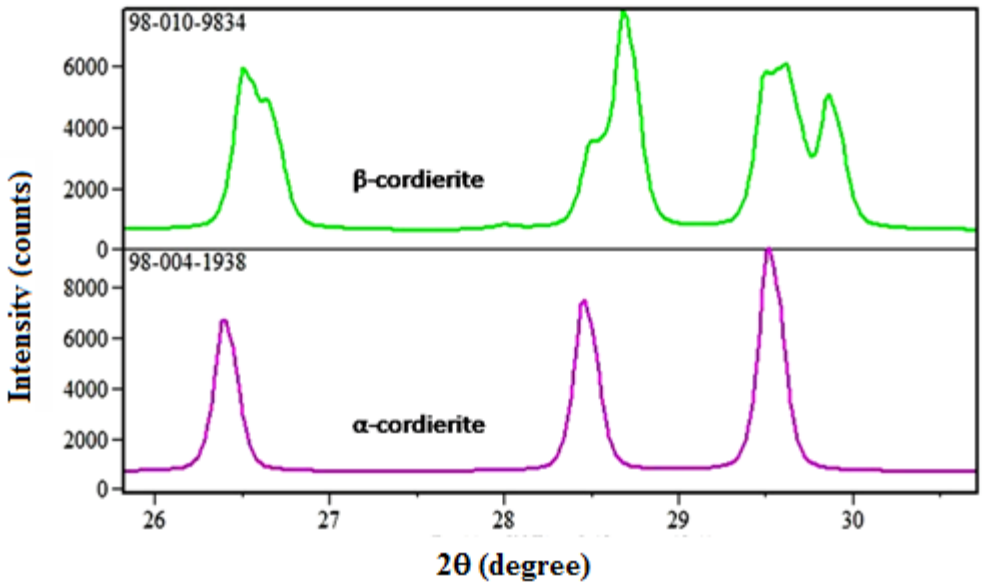

Figure 2.7 Diffraction pattern of hexagonal and orthorhombic cordierite can be distinguished after zooming at 2 Thetha 28-30^{o}

The identification peaks at 29-30° of the 2θ range reveals that the line corresponding to (211) planes has been divided into three orthorhombic peaks which are assigned to (151), (241) and (311) planes, respectively. This behavior shows the transformation of the polymorph with hexagonal symmetry, α-cordierite into polymorph with orthorhombic symmetry, β-cordierite. The polymorphic transformations between α-cordierite and β-cordierite are related to states of order

and disorder of one Al atom and five Si atoms in the tetrahedral rings of the structure. Hence, the material can exhibit all structural intermediates between α-cordierite and β-cordierite. Generally, Si and Al atoms are ordered in the β-cordierite structure and disordered in the α-cordierite structure. The ordering sequence of Al-Si in β-cordierite is shown in Figure 2.8. Numerous studies have been carried out to establish the mechanisms by which this Si and Al reordering take place, especially in the case of magnesium cordierite in which two stable polymorphs co-exist in non-equilibrium states. Gonzalez [44] in his research, reported that the first structure formed was hexagonal cordierite then finally it turned into orthorhombic cordierite by calcinations at 1400^{o}C. This means that the presence of specific polymorph is clearly dependent on the thermal treatment.

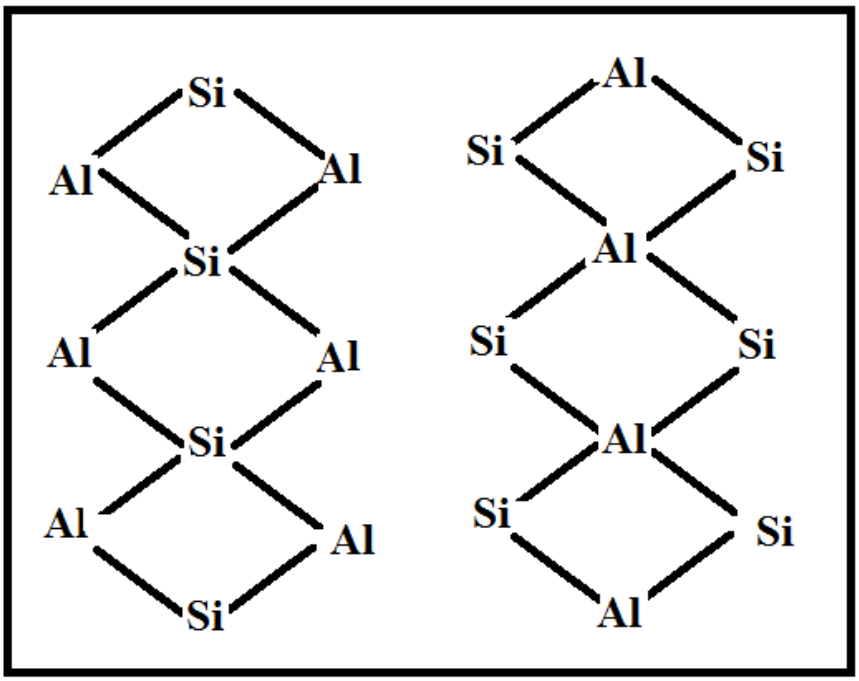

Figure 2.8 Al-Si ordering sequence in β-cordierite

The simplest way to determine the degree of transformation is by means of a parameter that represents the degree of distortion of the crystalline structure during its transformation from hexagonal to orthorhombic symmetry. Parameter denoted as Δ is named as distortion index and is calculated as Equation 2.1 [44].

$$\Delta = 2\theta_{131} - \left(\frac{2\theta_{151} + 2\theta_{421}}{2}\right) \quad \text{(Equation 2.1)}$$

Those phase with hexagonal crystal structure were found to be stable at the highest temperature (Δ=0). The orthorhombic phase corresponding to the previously named β-cordierite had a distortion index up to 0.25° and was named as low cordierite [44].

2.4 Common methods for synthesis of α-cordierite powders

As that of other crystalline ceramic phase, α-cordierite can be synthesized using various kinds of methods such as solid state reaction, sol-gel, non-hyrolytic sol-gel, hydrothermal, plasma sprayed, and crystallization of glass. However, the most common methods are by using solid state reaction, sol-gel and crystallization of glass.

2.4.1 Solid state reaction

α-cordierite can be obtained by solid state reaction at 1200-1350^{o}C using mixtures of starting materials (e.g. mixture of oxides, hydroxides, carbonates, kaolin, clays, talc, and chlorites) [10-13]. Grinding is necessary in order to achieve a homogeneous mixture of reactants,. The small particle sizes that are well mixed are needed in order to maximize the surface contact area. The number of particles in

contact may be increased by pelletizing the powders using a hydraulic press. Pelletizing decrease distance between particles, increase particle contact, and reduced large amounts of pore. Therefore, if enough thermal energy was supplied to the atoms or ion which exceed the energy barrier (activation energy), then the diffusion of atoms would occur, and particles are easily coalesce by material transport. Interstitials and subtitutional of ions or atoms occurs during diffusion in order to achieve electroneutrality.

Sintering temperature for single phase oxides typically fall in the range of 0.75-0.90 of the melting temperature (T_m) [46], and with a reasonable reaction time to overcome the lattice energy so that a cation can diffuse into a different site [44].

The progress of chemical change will depend on the area and defect structure of the contact areas between the reactant solids and the products when liquefaction did not occur. The progress of such chemical changes is strongly influenced by two factors: i) the contact interfacial area which is not dependent on the absolute reactant mass. For instance two large single crystals touching at a small area of interfacial contact may only yield a small amount of product compared to small mass of compacted fine powder with larger contact area, and ii) the ease of diffusion of reactants through the product layer which depends upon temperature and defect structure of the product layer. Thus, solid state reaction may vary considerably between different reactant samples, and dense α-cordierite phase in solid state reaction normally obtained at temperature of 1200^{o}C-1350^{o}C [47-49].

2.4.2 Sol-gel method

α-cordierite phase can also be obtained by sol-gel processes in which the components are proportionally mixed in liquid state with an orgonometallic precursor, producing a sol-gel system that generates the ceramic material when dried and calcined at high temperature. Sol-gel is a very attractive synthesis technique because of its ability to generate stoichiometric materials of high purity with good control over particle size. The products of the sol-gel process which having high surface area can be densified by sintering at much lower temperatures than conventional preparations.

Sol-gel techniques have been reported in the synthesis of cordierite powders using alkoxides and metal salt as the starting material[50]. In most cases tetraethylorthosilicate (TEOS) was used as a source of silicon. In general, sol-gel process involves a transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compound such as metal alkoxides [51-53]. The sol-gel process is well known for its capability to generate oxide glasses and ceramics. The sol-gel method involves hydrolysis of metal alkoxides and subsequent condensation to yield amorphous polymeric gels. The gels can then be dried with the help of drying control additives supercritically to form xerogels, ambigels or aerogels, respectively. The dried gels when heat-treated transform to yield crystalline oxide. Metal alkoxides ($M(OR)_n$) are compounds, where the metal species (M) are bound to organic carbon via oxygen [52, 54]. The alkoxy group (OR) in a metal alkoxide is a Lewis base which is an atomic or molecular species that

donates one pair electron and it undergoes hydrolysis to form a metal oxide or hydroxide as the Equation 2.2.

$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH$: hydrolysis (Equation 2.2)

Polymerization and condensation

$M(OH)_n + M(OH)_n \rightarrow (OH)_{n-1}\ M\text{-}O\text{-}M(OH)_{n-1} + H_2O$ (Equation 2.3)

$M(OH)_n + M(OH)_n \rightarrow (OH)_{n-1}\ M\text{-}O\text{-}M(OR)_{n-1} + ROH$ (Equation 2.4)

The sol-gel method can be generally utilized to generate crystalline or amorphous oxides depending on the experimental conditions such as pH in the solution, temperature and the amount of catalyst for inducing hydrolysis, etc. The sol-gel approach can provide amorphous or crystalline oxides of high purity, fine particle size and variable compositions. It has been very well exploited for synthesizing materials at lower temperature, which typically form at high temperatures using solid state reaction.

The disadvantage is due to the extreme moisture sensitivity of the alkoxide. In addition, microscopic inhomogeinity in the resultant gels and oxides due to different rates of hydrolysis for various alkoxides has been observed. Although the problem can be resolved by controlling the hydrolysis temperature, type of catalyst, concentration of alkoxides, and the amount of water. However, the process becomes more complex and is not practical for industrial applications who producing powders for bulk materials.

2.5 Crystallization of glass method

Glass-ceramic materials are polycrystalline solids that are embedded in an amorphous glass matrix. It was produced by a process referred to here as "devitrification or crystallization of glass. The first step towards the transition process involves conventional techniques for glass production, followed by crystallization under carefully controlled operating conditions. These post-treatment of amorphous glass would leads to the separation of a crystalline phase from the glassy parent phase.

Glasses are formed by melting the compounds above its melting temperature followed by cooling from the liquid state at rates fast enough without crystallization. Glass-ceramics have a unique microstructure, consisting of homogeneous pore free matrix with a very fine grain, and interwoven with residual glass phase. It properties is determined by the nature of crystalline phase, residual glass and microstructure. The composition of the parent glass and crystallization are extremely important to the final property of the glass. Glass exist in metastable state has a free energy higher than that corresponding crystalline phases of the same composition. For the purposes of attaining useful properties in a glass-ceramic, it is necessary to control the process from melting up to nucleation and growth of crystal. An understanding of nucleation and crystallization of glasses is important in order to crystallize glass with control microstructure. This is because nucleation and crystallization determine the total amount of crystalline phase devitrified from the glass upon heat treatment. Therefore, high degree of crystalline phase would be obtained if high fraction of nuclei formed and growth. Variation of nucleation and growth rate as a function of heat treatment

temperature would results in the formation of crystals with various sizes. The crystals with different size and different orientation can be observed through the size and the orientation of the grain. Meanwhile, the grain boundary of crystals demonstrates the imperfection between the crystals.

Crystallization of a glass involves the transition from the random structure of a liquid to the more ordered regular lattice of a crystalline solid. The driving force for crystallization, as with any phase transition, is by lowering the free energy of the system and in this case is by decreasing the entropy (amount of disordered). The ability of a glass to crystallize is determined by kinetic factors, and the tendency of the atoms to rearrange. Therefore, for the purpose of attaining useful property in glass, it is necessary to control the process, so that homogeneous glass can be formed easily and the glass will crystallize such that microstructure can be control by crystallization condition.

2.5.1 Crystallization process

The crystallization process consists of two major events, nucleation and crystal growth. Nucleation and crystal growth are necessary in order to transform the glass from the metastable state to stable state. Thus, understanding on nucleation and growth is importantsince the development of crystal would not occurr without the presence of nuclei.