## **CHAPTER 2**

## THEORY AND LITERATURE REVIEW

In this chapter, attention is equally focused on ferroelectric materials, glasses and glass-ceramics. As LiNbO<sub>3</sub> phase is one of the important ferroelectric materials, it is first necessary to describe the information background of ferroelectric materials. Moreover, the theory of glasses and glass-ceramics will be described. The relevant literature on chemical compositions, structure and properties of lithium niobate glassceramics are reviewed. Finally, the concept of nucleation, crystallization, control crystallization of glass for converting to glass-ceramics and its applications in glassceramics are then described in more detail.

## 2.1 Ferroelectric materials

Ferroelectric materials have a spontaneous electric polarization which can be reversed by an applied electric field [11, 12]. This phenomenon is called ferroelectricity which was discovered in 1920 by J. Valasek [13, 14] who was investigating the dielectric properties of Rochelle salt (NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.4H<sub>2</sub>O). Later on barium titanate (BaTiO<sub>3</sub>) was discovered to be ferroelectric in 1944 by A von Hippel and has been known as the most commonly ferroelectric material since then. Over the past 60 years, more than 250 materials that exhibit ferroelectric properties, some of the more common/significant materials include: lead titanate (PLZT) [15]. Even though most

ferroelectric materials do not have iron in their lattice, the prefix ferro, meaning iron was used to describe the property of the hysteresis loop, having similar nature to that of the hysteresis loop of ferromagnetic materials [16].

## 2.1.1 Properties

#### 2.1.1.1 Pyroelectric properties and spontaneous polarization

All ferroelectric materials are pyroelectric, however, not all pyroelectric materials are ferroelectric. Ferroelectric and pyroelectric materials are in a polar group and possess a spontaneous polarization or electric dipole moment. However, this polarization can be reoriented or reversed fully or in part by an applied electric field only in ferroelectric materials. Complete reversal of the spontaneous polarization is called "switching". Normally, the phase transition of ferroelectric to paraelectric phase (non-polar phase) occurred at the Curie temperature ( $T_c$ ). In generally, the direction of the spontaneous polarization conforms to the crystal symmetry of the material, but the reorientation of the spontaneous polarization is a result of atomic displacements. The magnitude of the spontaneous polarization is greatest at temperatures well below the Curie temperature and approaches zero as the Curie temperature is reached.

Figure 2.1 shows the type of polarization in materials. The linear polarization with an external electric field (Fig. 2.1 (a)) is found in dielectric materials. Paraelectric materials, demonstrate a more pronounced nonlinear polarization as shown in Fig. 2.1 (b). The electric permittivity can be found from the slope of the polarization curve which is a function of the external electric field. In addition to being nonlinear, ferroelectric materials possess a spontaneous

polarization (Fig. 2.1 (c)). The distinguishing feature of ferroelectrics from pyroelectrics that the direction of the spontaneous polarization can be reversed by an applied electric field, yielding a hysteresis loop.



Fig. 2.1 Polarization of (a) dielectric, (b) paraelectric and (c) ferroelectric. [16]

#### 2.1.1.2 Piezoelectric properties

Since all pyroelectric materials are piezoelectric, this means ferroelectric materials are inherently piezoelectric. In response to an applied mechanical load, this piezoelectric material produces an electric charge proportional to the load. Conversely, the materials generate a mechanical deformation in response to an applied voltage. Properties including the piezoelectric, dielectric and electro-optic coefficients may vary by several orders of magnitude in the narrow temperature band around the Curie temperature. Especially when compared to other temperature ranges, the changes to these coefficients are much more gradual. The piezoelectric coefficient is much greater in the region of the Curie temperature. Other properties such as dielectric strength and electro-optic properties also change markedly in the region of the Curie temperature when compared to other temperature ranges.

## 2.1.2 Applications [16]

The nonlinear property of ferroelectric materials is useful for making capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of two parallel plates of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value. This value especially reaches maximum when close to the Curie temperature. This allows ferroelectric capacitors to be small in size compared to other dielectric (non-tunable) capacitors of similar capacitance.

The hysteresis behavior of ferroelectric materials, having spontaneous polarization, offers an application in a memory function. Therefore, they are used to make ferroelectric RAM [17] for computers and RFID cards. In this case, ferroelectric

thin films are used which eases the switching process of the polarization as the high coercive field can be achieved with an applied moderate voltage. The reliability of the devices is greatly related to the interfaces, electrodes and sample quality [18].

All ferroelectric materials possess piezoelectric and pyroelectric properties inherently. Thus, the combined properties of memory, piezoelectricity, and pyroelectricity allow ferroelectric capacitors to be very useful devices, e.g. for sensor applications. Moreover, they can also be used in medical ultrasound machines (the capacitors generate and then listen to the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (a two dimensional array of ferroelectric capacitors used to detect the differences of temperature of the infrared image with high precision in a range of millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. In addition, the ferroelectric materials can be applied for the electro-optic modulators that can be used in the backbone of the internet.

Recent interest is also related to the ferroelectric tunnel junction (FTJ) in which a contact made of a nanometer-thick ferroelectric film is placed between metal electrodes. This ultra thin ferroelectric layer allows tunneling of electrons. Furthermore, a giant electroresistance (GER) switching effect may be achieved by the combination of piezoelectric and interface effects with a depolarization field.

Another possible application comes from the coupling effect of magnetic and ferroelectric ordering, known as multiferroics, which has been one of the most interesting topics among researchers [19-22].

#### 2.1.3 Lithium niobate (LiNbO<sub>3</sub>)

Lithium niobate is a colorless crystal, consisting of niobium, lithium, and oxygen atoms. It has trigonal crystal structure as shown in Fig. 2.2. Its crystal is transparent for wavelengths between 350 - 5500 nm and has a band gap of 4 eV. The melting point and density of this material are 1257 °C and 4.64 g/cm<sup>3</sup>, respectively, and is insoluble in water. These properties are also tabulated in Table 2.1. The optical properties of lithium niobate crystal can be improved by doping with magnesium oxide, as it increases the resistance to optical damage (also known as photorefractive damage) when doped above the optical damage threshold. Other available dopants are Fe, Zn, Hf, Cu, Gd, Er, Y, Mn and B [23, 24], provinding optical sources that can be modulated by traveling-wave waveguide modulators. As a result of the lack of inversion symmetry, lithium niobate crystals display the Pockels effect. Furthermore, this crystal exhibits birefringence effect, which is highly temperature dependent. Thus, the accurate heating of the crystal can be therefore used to achieve phase matching in the medium. In general, lithium niobate single crystals can be grown using the Czochralski process [25], which provides unique electro-optical, piezoelectric, photoelastic and nonlinear optical properties. They are strongly birefringence, which can be used in laser frequency doubling, nonlinear optics, Pockels cells, optical parametric oscillators, Q-switching devices for lasers, other acousto-optic devices, optical switches for gigahertz frequencies, etc. Consequently, it is an excellent material to manufacture optical waveguides. Additionally, lithium niobate is used extensively in the telecomunication market, for examples; in the mobile telephones and optical modulators, and it is also applied for surface acoustic wave devices. For some uses it can be replaced by lithium tantalate ( $LiTaO_3$ ) [26].

**Table 2.1** Basic properties of lithium niobate.[23, 27]





Fig. 2.2 Crystal structure of LiNbO<sub>3</sub> showing the octahedral oxygen coordination spheres of niobium. [28]

## 2.2 Glass

Glasses are classified in a familiar group of ceramics. Typical applications of glasses are containers, windows, lenses, and fiber-glass. Glasses are noncrystalline materials or are said to be amorphous or glassy [29] as is shown in Fig. 2.3, comparing the random amorphous structure of silica glasses and long range structure of silicon dioxide crystals. The compositions of several common glass materials are shown in Table 2.2 [30]. However, a typical glass is called soda-lime glass consisting of approximately 70 wt% SiO<sub>2</sub>, the balance being mainly Na<sub>2</sub>O (soda) and CaO (lime). One of the most important properties of these materials is transparency, resulting from complete lack of grain boundaries or inclusions which would cause the reflection of light.



**Fig. 2.3** Comparison of glass structure: (a) random amorphous structure and (b) ordered crystalline structure. [31]

| Glass Type                    | Composition (wt %) |                   |       |                                |   |  | Characteristics   |
|-------------------------------|--------------------|-------------------|-------|--------------------------------|---|--|---|
|                               | SiO <sub>2</sub>   | Na <sub>2</sub> O | CaO   | Al <sub>2</sub> O <sub>3</sub> | <b>B</b> <sub>2</sub> <b>O</b> <sub>3</sub> | Other  |   |
| Fused Silica                  | >99.5              | -                 | -     | - (                            |   |  | High melting temperature, very low coefficient of expansion (shock resistant) |
| 96% Silica (Vycor)            | 96                 |                   | -     | -                              | 4   |  | Thermally shock and chemically resistant-<br>laboratory ware                  |
| Borosilicate (Pyrex)          | 81                 | 3.5               |       | 2.5                            | 13  |  | Thermally shock and chemically resistant-<br>ovenware                         |
| Container (soda-lime)         | 74                 | 16                | 5     | 1                              | Ζ- ι  | 4MgO   | Low melting temperature, easily worked, also durable                          |
| Fiberglass                    | 55                 | ຮ                 | 16    | 15                             | 10  | 4MgO   | Easily drawn into fibers-glass-resin composites                               |
| Optical flint                 | 54                 | D<br>ht           | Ċ     | Ь                              |   | 37PbO,<br>8K <sub>2</sub> O                                | High density and high index of refraction-optical lenses                      |
| Glass-ceramics<br>(Pyroceram) | 43.5               | 14                | i _ 8 | B 30                           | 5.5   | 6.5TiO <sub>2</sub> ,<br>0.5As <sub>2</sub> O <sub>3</sub> | Easily fabricated, strong and resists thermal shock-<br>ovenware              |

 Table 2.2 Composition and characteristics of some common commercial glasses. [30]

#### 2.2.1 Theory of glass

The most widely used definition of a glass, proposed by the ASTM, is "a glass is an inorganic product of fusion that has cooled to a rigid condition without crystallizing" [32]. Organic substances, for examples glucose and glycerol, would not be included in this definition, although they can be supercooled to a rigid condition without crystallizing. Moreover, such a definition would exclude amorphous substances which are not prepared by melt cooling methods, but by other techniques, such as vacuum evaporation [1].

A precise definition of glass is that "a glass or a substance in the glassy or vitreous state, is a material, formed by cooling from the normal liquid state, which has shown no discontinuous changes (such as crystallization or separation into more than one phase at any temperature) but has become more or less rigid through a progressive increase in its viscosity" [1]. This definition regards viscosity as defining a natural boundary to the glassy state. It is useful because any materials cooled below its liquid state, but whose viscosity has not yet reached this limiting value, is called a super-cooled liquid. There is no exact limiting value for viscosity but it can be assumed that the viscosity of the melt at the transformation temperature should be greater than about  $10^{13}$  poises.

Glasses are characterized by many properties which reflect their liquid-like structures. One of the most important properties of glass is transparency, resulting from complete lack of grain boundaries or inclusions, which would cause the reflection of light. The property is usually found in the liquid state rather than in the solid crystalline state. The relationship between liquid and solid can give a clearer understanding of the origin of the structure of a glass. The arrangement of atoms in a liquid has shortrange order while that of a crystalline solid has both short-range and long-range order showing that the regularity in the solid is almost complete. Thus, a glass, which has a liquid-like structure, exhibits a lack of long-range periodic order. Moreover, the X-ray diffraction patterns of glass contain a few broad features reflecting the short-range radial distribution of atoms while that of a crystalline substance has sharp lines indicating the long-range 3D order. Glasses have broad melting behavior unlike the sharp melting points of crystalline solids.

These phenomena, which occur during the cooling of melts, are very important for understanding the relationship between the glassy state, normal liquid and solid state. Fig. 2.4 shows the relationship between these states by means of a volume- temperature diagram. This diagram can also be presented in terms of an enthalpy temperature because volume and enthalpy behave in a similar manner.

The liquid has a structure characteristic of the temperature at which the melt is held and, during cooling, the atomic structure of the melt will slowly change but still keep the characteristic short-range order of the primary liquid. In general, when melt is cooled below the melting temperature  $(T_m)$ , crystallization occurs and it becomes solid. As a rapid decrease of enthalpy appropriate value is occurred the crystal. On continued cooling, the enthalpy will decrease slowly controlled by the heat capacity of the crystal. However, if the liquid can be cooled below the melting point by avoiding crystallization, there will be an undercooling of the melt to give a supercooled liquid. No discontinuous rearrangement happens in this case as the temperature decreases, the overall enthalpy gradual changes. Further cooling produces deviation from the equilibrium line since the viscosity of the melt greatly increases, inhibiting atom movement, leading to difficulty in the rearrangement of atoms in the equilibrium liquid structure. Then as the temperature decreases, the viscosity increases rapidly, resulting in frozen-in, liquid-like structure. The slope after this is determined by the heat capacity of the frozen liquid. The glass transformation region, as it appears in the graph, may be defined by the temperature region joining the equilibrium liquid state and the frozen liquid state. Hence, the frozen liquid is a glass



Fig. 2.4 Effect of temperature on the enthalpy of a glass forming melts. [After Varshneya, A.K [35]]

As shown in Fig. 2.4, the intersection point between the glass and supercooled liquid lines is the fictive temperature ( $T_F$ ), which may be defined as "the temperature at which the glass would find itself in equilibrium if suddenly brought to it from its given state" [33]. The structure of an equilibrium liquid at this temperature is similar to the structure of glass. Moreover,  $T_F$  can be changed by thermal history such as cooling rate. A high cooling rate freezes the liquid into a glassy state at lower density and higher specific volume than a lower cooling rate. The glass formed by slow cooling has a tendency to be more stable than that of fast cooling. This is because the atomic arrangement of the slow cooled glass is closer to that characteristic of the equilibrium liquid than the more rapidly cooled glass [33, 35-36].

## 2.2.2 Raw materials for glass melting

In general, glasses are either produced from high-quality, chemically pure components or from a mixture of far less pure minerals. Research specimens, optical glasses and many glasses used for low-volume, high-technology applications are produced using those chemicals we might routinely encounter in any chemical laboratory. Bulk commercial products, on the other hand, are produced from minerals, which typically have names and compositions which are not familiar to the novice.

Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis on their role in the process: glass former, flux, property modifier, colorant and fining agent. The same compound may be classified into different categories when used for different purposes. Alumina, for example, serves as a glass former in aluminate glasses, but is considered as a property modifier in most silicate glasses. Arsenic oxide may be either a glass former or a fining agent, depending upon the purpose for which it has been added to the batch.

The most essential component of any glass batch is always the glass former. Every glass contains one or more components which serve as the primary source of the structure. While these components are commonly designated as glass formers, they are also called "network formers or glass forming oxides" [33] in many oxide glasses. The identity of these components usually serves as the basis for the generic name used for the glass. If most of the glass former present in a specific sample is silica, for example, that glass is called a silicate. If a significant amount of boric oxide is also present in addition to silica, the sample is termed a borosilicate glass.

The primary glass formers in commercial oxide glasses are silica (SiO<sub>2</sub>), boric oxide (B<sub>2</sub>O<sub>3</sub>) and phosphoric oxide (P<sub>2</sub>O<sub>5</sub>) which all readily form single component glasses. A large number of other compounds may act as glass formers under certain circumstances, including GeO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, TeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>. With the exception of GeO<sub>2</sub>, these oxides do not readily form glasses by themselves unless very rapidly quenched or vapor deposited, but can serve as glass formers when mixed with other oxides. The elements S, Se and Te act as glass formers in chalcogenide glasses. Although halide glasses can be made in many systems, with many different compounds acting as glass formers, the two most common halide glass formers are BeF<sub>2</sub> and ZrF<sub>4</sub>.

Although the number of possible glass compositions is effectively unlimited, the vast bulk of commercial glasses are based on silica as the glass former. While silica itself forms an excellent glass, with a wide range of applications, the use of pure silica glass for bottles, windows and other bulk commercial application would be prohibitively expensive due to the high melting temperature (> 2000 °C) required to produce vitreous silica. Production of silicate glasses requires the addition of a flux to reduce the processing temperature to within practical limits, e.g. < 1600 °C. The most common fluxes are the alkali oxides, especially Na<sub>2</sub>O and PbO. Most commercial glasses contain soda, including those used for containers and window glasses. Potassium oxide is also used extensively in commercial glasses, while lithium oxide is used in a number of commercial glass-ceramics. Rubidium and cesium oxides are frequently used in the laboratory, for studies of trends in behavior due to changes in the identity of the alkali oxide present in glasses, but are rarely used in commercial products due to their high cost. PbO, which is an excellent flux, is becoming much more limited in use due to concerns regarding the toxicity of heavy metals. PbO is especially useful in dissolving any refractory or other impurity particles which might otherwise result in flaws in the final glass.

While the addition of fluxes to silica leads to a decreased cost of glass formation, the addition of large amounts of alkali oxides results in serious degradation of in many properties. In particular, the chemical durability of silicate glasses containing large concentrations of alkali oxides is degraded to the point where they can no longer be used for containers, windows or insulation fibers. The property degradation is usually countered by the addition of property modifiers, which include the alkaline earth and transition metal oxides, and, most importantly, aluminum oxide (alumina). While these oxides partially counter the reduction in processing temperature obtained by the addition of fluxes, they also improve many of the properties of the resulting glasses. The properties can thus be modified, or adjusted, by careful control of the amount and concentration of these oxides to obtain precisely the desired results. Since many of these oxides are actually very weak fluxes for silica, and the property modifiers are usually added in lesser quantities than the fluxes, their use does not lead to excessively high processing temperatures.

Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the 3d transition metals or the 4f rare earths. Uranium oxides were once used as colorants, but their radioactivity obviously reduces their desirability for most applications. Gold and silver are also used to produce colors by formation of colloids in glasses. Colorants are only used if control of the color of the glass is desired, and are usually present in small quantities. Iron oxides, which are common impurities in the sand used to produce commercial silicate glasses, act as unintentional colorants in many products. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants.

Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, sodium chloride (NaCl), fluorides such as CaF<sub>2</sub>, NaF and Na<sub>3</sub>AlF<sub>6</sub> and a number of sulfates. These materials are usually present in very small quantities (< 1 wt %) and are usually treated as if they have only minor effects on the properties of the final glasses. Their presence, however, is essential in many commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product [33, 37].

#### 2.2.3. Atomic hypothesis of glass formation

In 1926, Goldschmidt pointed out that the glass forming ability of an oxide might be related to the arrangement of the oxygen ions around the cations in order to form the unit cell of the crystal structure. By geometrical considerations, it could be shown that in an oxide M<sub>x</sub>O<sub>y</sub>, coordination of M by O would equal four if the radius ratio R<sub>M</sub>/R<sub>0</sub> is in the range of 0.225 to 0.414. The most probable arrangement of atoms in this case is tetrahedral with the oxygen at all corner positions and the cation at the central position. Furthermore, he found that many glass forming oxides, such as SiO<sub>2</sub>, GeO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>, have tetrahedral arrangements in the crystalline state and this can be a criterion of glass forming ability. However, this postulate is not universally true so Zachariasen (1932) further developed the random network theory of glass structure. He suggested that, as in the crystal, the atoms in a glass must be linked in the form of a three-dimensional network but the arrangement of the structure in glass could not be long range ordered as in a crystal. As a result of this, the X-ray diffraction (XRD) pattern of a glass is not sharp like that of the crystal. He also deduced that the energy content of a substance in the glassy state must be slightly greater than that of the corresponding crystal network. Therefore, it could be assumed that the units of structure in a glass must be similar to those in the crystal. However, in the glass there is distribution of the bond angles so that the oxides form a random network, which is a non-periodic structure [38].

#### 2.2.4 Nucleation and crystallization

The diagram presented in Fig. 2.5 shows the types of nucleation and crystallization, which usually occur in glasses.

The descriptions of each transformation are presented as follows:

Crystallization is the process by which crystals are generated from the short range ordered liquid structure. The composition of a crystalline phase might or might not be the same as the original liquid [39].

- Surface crystallization is the growth of crystals from the glass/atmosphere interphase and usually growing perpendicular to this surface [40, 41].

Volume crystallization is the growth of crystal, from 'nucleation sites' in the body of the mineral. There are two types of the nucleation. The first type is heterogeneous nucleation where the initiating sites are pre-existing surfaces such as dust particles, crucible wall, etc. The second type is homogeneous nucleation where the nuclei are forming spontaneously within the melt [41].

- Spinodal decomposition is the separation of a non-crystalline phase limited by diffusion only. This separation occurs in a region of the separation of two phases where there is no energy barrier to nucleation [42].

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Fig. 2.5 Diagram of nucleation and crystallization. [After Paul A. [42]]

Devitrification is the growth of crystals in glasses and, to make a glass, this phenomenon must be prevented. However, devitrification is important in the glass-ceramic process. This process must be controlled in order to have the correct microstructure and properties of final materials [43, 44]. Crystallization is the consequence of two individual kinetic processes, which are nucleation and crystal growth. In terms of nucleation, two contributions concerned with the stability of a particle in homogeneous nucleation are the free energy and the interfacial energy. At the melting point, the free energy of a material is the same in both the crystalline and liquid forms. The melt of a single element is cooled below the melting point, the crystalline form will have a lower free energy and, if nuclei available, the liquid will crystallize.

The following equation shows the free energy change for the nucleation.

$$\Delta G = -\frac{4}{3}\pi r^3 \cdot \overline{\Delta G} + 4\pi r^2 \sigma \qquad (2.1)$$

Where  $\Delta G$  is the change in free energy per unit volume for the crystal-liquid transformation,  $\frac{4}{3}\pi r^3$  is the volume of the nucleus (*r* is the radius of nucleus or crystal),  $\sigma$  is the surface tension or interfacial energy and  $4\pi r^2$  is the surface area.  $r^* = \frac{2\sigma}{\Delta G}$  is a critical radius where  $\frac{d(\Delta G)}{dr} = 0$ . If particles have a radius smaller than  $r^*$ , they are called embryos,  $\frac{d^2(\Delta G)}{dr^2}$  is positive and thus they are unstable. On the other hand, if they have radius greater than  $r^*$ , they are called nuclei,  $\frac{d^2(\Delta G)}{dr^2}$  is negative and therefore they are stable. The rate of nucleation is controlled by the production of critical sized nuclei per unit volume and the rate at which atoms attach to the embryo. It can be shown in this following equation:

$$I = N_s \frac{kT}{h} \exp\left(-\frac{\Delta G_a}{kT}\right) \cdot N \exp\left(-\frac{\Delta G^*}{kT}\right)$$
(2.2)

The term,  $N_s \frac{kT}{h} \exp\left(-\frac{\Delta G_a}{kT}\right)$  is the number of atoms crossing the interface

per second, where  $N_s$  is the number of atoms adjacent to the surface of embryos, h is Planck's constant,  $\frac{kT}{h}$  is the vibrational frequency of the atom and  $\Delta G_a$  is called the kinetic barrier to nucleation. In other words, the first term corresponds to the diffusion of matter during the formation of the nucleus by Turnbull and Cohen [45]. The second term  $(N \exp\left(-\frac{\Delta G^*}{kT}\right))$  is the probability of forming a nucleus larger than the critical size at the temperature, where N is the number of atoms per unit volume and  $\Delta G^*$  is

size at the temperature, where N is the number of atoms per unit volume and  $\Delta G$  is the thermodynamic barrier to nucleation.

In terms of crystal growth, the rate of crystal growth is the rate at which atoms arrive and remain at the surface of the nucleus. The growth rate of the crystal (u) is given as follows:

$$u = \lambda v_0 \exp\left(-\frac{\Delta G_a}{kT}\right) \cdot \left(1 - \exp\left(-\frac{\Delta G}{RT}\right)\right)$$
(2.3)

Where  $\lambda$  is the average interatomic spacing between atoms in the liquid and nucleus (crystal),  $v_0$  is the frequency at which the atom in the liquid vibrates due to thermal energy,  $\Delta G_a$  is the activation energy for an atom in the liquid to pass through the interface between the crystal and surrounding liquid, *R* is the gas constant and  $\Delta G$ is the energy change when an atom crosses the interface to the crystal.

The first term  $\lambda \upsilon_0 \exp\left(-\frac{\Delta G_a}{kT}\right)$  gives the probability of an atom having sufficient thermal energy to leave the liquid and join the nucleus. The second term  $\left(1-\exp\left(-\frac{\Delta G}{RT}\right)\right)$  is the factor, which is formed by the consolidation of the reduction

in energy when the atom has crossed the interface to the crystal [42].

The rates of homogeneous nucleation and crystal growth in a viscous liquid are shown in Fig. 2.6. From this figure, it can be noticed that, at the temperature at which the maximum nucleation rate takes places, the maximum possible number of crystal nuclei will be produced in a given length of time. Therefore, the optimum nucleation temperature  $(T_n)$  can be selected for the production of glass-ceramics.

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Fig. 2.6 Rates of homogeneous nucleation and crystal growth in a viscous liquid. [34]

A glass is a metastable substance so either a low rate of crystal growth or a low rate of nucleation may encourage glass formation. In a normal glass, heterogeneous nucleation does not often occur because the glass melt is a good solvent for foreign particles. In addition, the homogeneous nucleation of a glass forming liquid is difficult to achieve since the activation energy of diffusion is relatively high even at high temperatures. As a result of this, it is possible to cool the glass melt through the critical temperature zone in which nucleation might take place. It is important to consider the time which glass spends in this critical zone of temperature and glasses must usually be cooled quite quickly through this zone [1, 34, 42].

## 2.2.5 Controlled crystallization

A controlled heat treatment is aimed at converting glass into a glass-ceramics, which will has better properties than the original glass. Fig. 2.7 shows the various stages of the heat treatment process, which is presented as an idealized heat treatment schedule for a glass-ceramics.

The optimum nucleation temperature should be between the glass transition temperature and a temperature 50 °C lower than this. In many instances, the nucleation stage can be omitted. Sufficient nucleation can be achieved during heating the glass to the crystallization temperature at which crystals grow upon the nuclei [46].



Total heat treatment time

Fig. 2.7 Schematic diagram of idealized heat treatment; x: heating rate, y: heat treatment temperature and z: dwell time. [After Werner V. [46]]

## 2.3 Glass-ceramics

#### 2.3.1 History

Glass-ceramics may be defined as polycrystalline solids prepared by controlled crystallization of glasses. Crystallization can be achieved by putting appropriate glasses through a regulated heat treatment schedule that causes nucleation and growth of crystal phases inside the glass. However, a small amount of residual glass often occurs and strongly affects a number of important properties of glassceramics [1].

It has been known for centuries that most glasses can be crystallized if they are subjected to heating for a sufficient length of time at a suitable temperature. There was no systematic development until the discovery of the first true glass-ceramics in 1957 by Dr. Stanley Donald Stookey [47, 48] at Corning Glass Works. He found that it is possible to form glass objects by conventional methods and transform them to fine-grained ceramics by heat treatment. After that, he successfully invented photochromic glasses, machinable glasses and polychromatic glasses. These products have far more mechanical strength than in their original forms. The effective nucleating catalyst used in most of Stookey's system was  $TiO_2$  and in 1970 McMillan *et al* [49] reported that the use of metallic phosphates (P<sub>2</sub>O<sub>5</sub>) could also promote controlled crystallization in glasses. In addition to these, other oxides, such as  $ZrO_2$ ,  $SnO_2$ ,  $CrO_3$  and  $V_2O_5$  [42] were later discovered to be effective nucleating agents.

#### 2.3.2 Theory of glass-ceramics

Important aspects of glass-ceramics are nucleation and crystallization. Glass forming liquids are generally very viscous; therefore, processes of diffusion and atomic rearrangement are slow, which enables control of nucleation and crystal growth. The rapid quenching process can be applied to the viscous liquids in order to avoid the crystallization process during cooling and the resulting glass product can be used for further investigation of glass-ceramics. Another important phenomenon is amorphous phase separation, which can be important in both glass-ceramics formation and the stability of glasses. Because a glass melt is a good solvent for most oxides, a wide range of composition can be obtained, leading to the potential formation of glass-ceramics containing many crystal types, such as metastable phases and solid solutions within a variety of chemical environments. The ultra fine grains, typically less than one micrometer of glass-ceramics provide valuable materials properties, such as good mechanical strength and good fracture toughness. These ultra fine grains make glass-ceramics stronger than ordinary glasses and conventional ceramics. Due to this, it is possible to control the degree of crystallinity in glassceramics, leading to the studies of mechanical failure and the investigation of the properties, involving diffusion, for example: ionic conductivity.

Normally, glass-ceramics are not transparent to visible light. However, transparent glass-ceramics can be derived if the crystals present are smaller than the wavelength of visible light or by minimizing the difference between the refractive indices of the parent glasses and crystals [50].

## 2.3.3 Applications

Apart from the early applications of glass-ceramics by Stookey and coworkers, more recent studies include:

- Glass-ceramics from the systems  $Li_2O \cdot Al_2O_3 \cdot SiO_2$  [51] and  $CaO \cdot Al_2O_3$ 

 $\cdot$  SiO<sub>2</sub> [52] having thermal expansion values near zero, can be used as high temperature cookware, cooker hot plate, laboratory bench tops and rotary heat exchangers for gas turbines.

- The magnesia-alumina-silica type [53] or Cordierite glass-ceramics [54] and glass-ceramics derived from  $ZnO \cdot Al_2O_3 \cdot SiO_2$  with addition of CaO, BaO or SrO, [55] have low dielectric loss, high strength, good thermal shock resistance, high rain erosion resistance and are transparent to microwaves. They can be used in the production of radar for missiles.

- Machinable mica based glass-ceramic materials can be produced by crystallization of fluorophlogopite; such as  $KMg_3AlSi_3O_{10}F_2$  in glasses having wt % compositions of 30-50 % SiO<sub>2</sub>, 3-20 % B<sub>2</sub>O<sub>3</sub>, 4-12 % K<sub>2</sub>O, 15-25 % MgO and 4-10 % F or K<sub>2</sub>O · B<sub>2</sub>O<sub>3</sub> · Al<sub>2</sub>O<sub>3</sub> · SiO<sub>2</sub> · MgO · F for dental restoration [56].

- Glass-ceramics can be used in the biomedical field; such as for the production of artificial teeth from  $Li_2O \cdot ZnO \cdot SiO_2$  glass systems. These products have a good acid resistance, high abrasion resistance and close thermal expansion matching between the glass-ceramics and the real tooth [57].

- Transparent glass-ceramics can be produced from many glass systems, such as  $Li_2O \cdot MgO \cdot ZnO \cdot Al_2O_3 \cdot SiO_2$  [58],  $LiO_2 \cdot MgO \cdot Al_2O_3 \cdot SiO_2$  [59] and  $ZnO \cdot Al_2O_3 \cdot ZrO_2 \cdot SiO_2$  [60] with the corresponding major crystalline phases present being  $\beta$ -eucryptite, mullite and spinel respectively. They can be used in large optical telescopes (eucrypite type) and as the envelope material for high-performance lamps (mullite and spinel type).

- Transparent ferroelectric glass-ceramics can be achieved with a variety of precipitated crystalline phases; such as BaTiO<sub>3</sub> [61], Pb<sub>3</sub>MgNb<sub>2</sub>O<sub>9</sub> (PMN) [62], Pb<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> [63] and LaBGeO<sub>5</sub> [64]. These glass-ceramics have electro-optical effects so they can be used in optical devices.

- Several transparent glass-ceramic systems can be doped with transition elements; such as alkali gallium silicate  $(3.4Na_2O \cdot 3.3K_2O \cdot 13.3Ga_2O_3 \cdot 80.0SiO_2)$ doped with 1.0 mol% NiO which have very broad emission and long fluorescent lifetime in the near-infrared region. These hybrid optical materials preserve both glass and crystal properties. The glass matrix is transparent and can be easily drawn into fibers; while nanocrystalline precipitates host optically active dopants, which may have very high quantum efficiency for emission.

#### 2.4 Literature review

Many researches and development in the field of glass-ceramics are driven by new compositions with specific properties and device applications. The most improved glass-ceramics were developed by introducing selected crystallization of ferroelectric materials which have interesting dielectric and electro-optical properties for electro-optical applications. But the original glass-ceramics are still used as cookware and spark plug insulators because they are more resistant to thermal shock and are also stronger at high temperatures than typical glasses [66]. Thus, some closely related works are reviewed as follows:

## 2.4.1 Lithium-based glasses and glass-ceramics

2.4.1.1 Crystallization and glass formation in  $50Li_2O \cdot 50Nb_2O_5$  and  $25Li_2O \cdot 25Nb_2O_5 \cdot 50SiO_2$  [6]

In 1997, Zeng *et al* studied crystallization and glass formation in  $50Li_2O \cdot 50Nb_2O_5$  and  $25Li_2O \cdot 25Nb_2O_5 \cdot 50SiO_2$  using the conventional melting method. They found that morphology of  $50Li_2O \cdot 50Nb_2O_5$  glass-ceramics appeared to have dendrites growth on the surface as shown in Fig. 2.8. No secondary phases were identified from the XRD patterns except for LiNbO<sub>3</sub> as shown in Fig. 2.9.



Fig. 2.8 Micrographs of surface morphologies of 50Li<sub>2</sub>O · 50Nb<sub>2</sub>O<sub>5</sub> glass-ceramics:
(a) one-side quenching and (b) two-side quenching. [6]



Fig. 2.9 XRD patterns of  $50Li_2O \cdot 50Nb_2O_5$  glass-ceramics: (a) one-side quenching and (b) two-side quenching. [6]

 $25Li_2O \cdot 25Nb_2O_5 \cdot 50SiO_2$  glass-ceramics did not have a crystalline phase but when it brought about heat treatment at 800 °C for 30 min, it could establish LiNbO<sub>3</sub> crystalline phase on the surface. Both glass-ceramics contain LiNbO<sub>3</sub> crystalline phase which were detected by XRD technique as shown in Fig. 2.9 and Fig. 2.10.



Fig. 2.10 XRD patterns of  $25Li_2O \cdot 25Nb_2O_5 \cdot 50SiO_2$  glass-ceramics: (a) asquenching and (b) heat treatment at 800 °C for 30 min. [6]

2.4.1.2 Lithium niobate ferroelectric material obtained by glass crystallization [67]

In 1997, Todorovic and Radonjic studied lithium-niobate ferroelectric materials obtained by glass crystallization. They prepared transparent glasses and glass-ceramics by the heat treatment method as containing LiNbO<sub>3</sub> crystals in Li<sub>2</sub>O · Nb<sub>2</sub>O<sub>5</sub> · SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> system. XRD and SEM analyzes of the glass-ceramic samples  $(29.2Li_2O \cdot 28.2Nb_2O_5 \cdot 37.2SiO_2 \cdot 5.4Al_2O_3; L-4)$  are shown in Table 2.3. The glass sample L-4/D had values of dielectric constant ( $\epsilon_r$ ) = 155-185 at frequency of 1 kHz,

room temperature and refractive index (n) = 1.84-1.93 because it contains intensively crystalline LiNbO<sub>3</sub>.

 Table 2.3 Heat treatment conditions, visual appearance and phase compositions of the sample L-4. [67]

| Sample<br>notation | Temperature<br>(°C) | Time<br>(min) | Appearance and phase compositions                         |
|--------------------|---------------------|---------------|---|
| L-4/A              | 500-600             | 10            | Transparent, glassy-phase                                 |
| L-4/B              | 610                 | 10            | Transparent, phase separation on the scale 20-            |
|                    |                     |               | 50 nm   |
| L-4/C              | 620                 | 10            | Transparent, nucleation of LiNbO <sub>3</sub> , 50-150    |
|                    |                     |               | nm  |
| L-4/D              | 650                 | 10            | Transparent, crystallization of LiNbO <sub>3</sub> , 150- |
|                    |                     |               | 350 nm  |
| L-4/E              | 650                 | 30-60         | Opaque, crystallization of LiNbO <sub>3</sub> , 800-1000  |
|                    |                     |               | <sup>nm</sup> แก่ ถึง เมือง ใหม่                          |
| L-4/F              | 700-900             | 10            | Opaque, crystallization of LiNbO <sub>3</sub> , 800-1000  |
|                    |                     |               | hiang Mai University                                      |
|                    | rigi                | h t           | s reserved  |

2.4.1.3 Evolution of ferroelectric LiNbO<sub>3</sub> phase in a reactive glass matrix (LiBO<sub>2</sub>  $\cdot$  Nb<sub>2</sub>O<sub>5</sub>) [68]

In 2005, Prasad and Varma studied the evolution of ferroelectric LiNbO<sub>3</sub> phase in a reactive glass matrix (LiBO<sub>2</sub> · Nb<sub>2</sub>O<sub>5</sub>). X-ray diffraction studies were performed at room temperature on the as-quenched and heat-treated samples to confirm their amorphous and crystalline nature respectively as illustrated in Fig. 2.11. The XRD patterns of heat-treated sample at high Nb<sub>2</sub>O<sub>5</sub> content (x = 20) showed LiNbO<sub>3</sub> and LiNb<sub>3</sub>O<sub>8</sub> phases, while heat-treated sample at low Nb<sub>2</sub>O<sub>5</sub> content (x = 5) also showed other phases that are LiBO<sub>2</sub> and Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> phases. It is also observed that the intensity of the peaks corresponding to the LiNb<sub>3</sub>O<sub>8</sub> which formation increases with increasing in the Nb<sub>2</sub>O<sub>5</sub> content.

SEM was done to visualize the microstructural changes that follow, on increasing the heat treatment temperature as shown in Fig. 2.12 which showed the scanning electron micrographs recorded for the samples of the composition  $85LiBO_2$ - $15Nb_2O_5$  heat-treated at 475, 500, 600 and 650 °C. Nevertheless, the samples heat-treated at higher temperatures (> 500 °C) revealed the presence of voids/micro cracks as depicted in the inset of Fig. 2.12(c). With increase in heat treatment temperature the volume percentage and the connectivity of these voids/micro cracks were found to increase resulting in low density composites which are not favorable for electrical applications as they were found leakier than the samples without voids (samples heat-treated at 500 °C). The void/micro crack formation in the samples heat-treated at higher temperatures was attributed to the thermal expansion mismatch to a considerable extent in the crystalline phases involved.



Fig. 2.11 XRD patterns of the as-quenched ((a)-(b)) and the samples heat-treated at

500 °C for 3 h ((c)-(f)). [68]

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Fig. 2.12 SEM records of the samples heat-treated at different temperatures: (a) 475 °C, (b) 500 °C, (c) 600 °C and it shows voids/micro crack formation and (d) 650 °C. [68]

## 2.4.2 Others ferroelectric-based glasses and glass-ceramics

2.4.2.1 Crystallization of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> from glasses in the system Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> [69]

In 1997, Kirsten and Christian studied crystallization of  $Bi_4Ti_3O_{12}$  from glasses in the system  $Bi_2O_3/TiO_2/B_2O_3$ . They found that the ferroelectric  $Bi_4Ti_3O_{12}$ phase is formed by heat treatment method at temperatures in the range of 500 to 700 °C, after treatments at 600 °C; maximum crystal content was obtained. The variation of the glass composition affected the microstructure: the smaller the content of  $B_2O_3$ , the smaller are the crystallites formed and the larger their quantity. Some of these glass-ceramics contained crystals with plate-like morphology.

2.4.2.2 Crystallization of Bi<sub>3</sub>TiNbO<sub>9</sub> from glasses in the system Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub>/B<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> [70]

In 1999, Kirsten and Christian also studied crystallization of  $Bi_3TiNbO_9$  from glasses in the system  $Bi_2O_3/TiO_2/Nb_2O_5/B_2O_3/SiO_2$ . But in this work  $SiO_2$  was also added, because it is interconnected and caused glass-ceramics to have a higher relative dielectric constant. Although these glass-ceramics also contained other crystalline nonferroelectric phases, such as  $Bi_7Ti_4NbO_{21}$ . They found that the ferroelectric  $Bi_3TiNbO_9$ phase was formed by thermal treatment at temperatures in the range of 500 to 860 °C, the quantity and grain size of crystalline phase depends on the crystallization temperature and glass former ( $B_2O_3$ ).

2.4.2.3 Crystallization of ferroelectric bismuth vanadate in  $Bi_2O_3 \cdot V_2O_5$  $\cdot SrB_4O_7$  glasses [71]

In 1998, Shankar and Varma studied crystallization of ferroelectric bismuth vanadate in  $Bi_2O_3 \cdot V_2O_5 \cdot SrB_4O_7$  glasses. The as-quenched samples were confirmed to be amorphous by the XRD technique. Hence, they were heat-treated at 683 K for 12 h and the crystals were indexed to an orthorhombic bismuth vanadate,  $Bi_2VO_{5.5}$  (BiV) phase as shown in Fig. 2.13. They found that the relative dielectric constant ( $\varepsilon_r$ ) of the glass-ceramics increases with increasing dwell time at 683 K and the refractive indices are in the range from 1.86 to 2.17.



**Fig. 2.13** XRD patterns of the as-quenched samples ((a)-(c)) and the glass-ceramic samples ((d)-(f)). [71]

# 2.4.2.4 BiO<sub>1.5</sub> · BO<sub>1.5</sub> · GeO<sub>2</sub> glass system and crystallization of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> phase [72]

In 2000, Nara *et al* studied the  $BiO_{1.5} \cdot BO_{1.5} \cdot GeO_2$  glass system and crystallization of  $Bi_4Ge_3O_{12}$  (BGO) phase. For samples crystallized after heat treatment, most of the XRD peaks can be assigned to the BGO and  $Bi_6B_{10}O_{24}$ crystalline phases as shown in Fig. 2.14. Two types of analysis of the crystallized sample were performed. Surface observation detected prismatic crystals which assumed that they are  $Bi_6B_{10}O_{24}$ . On the broken sample, the microphotographs displayed the presence of crystals with a pyramidal shape identified as BGO as shown in Fig. 2.15.



Fig. 2.14 XRD pattern of the glass sample (45BiO<sub>1.5</sub> · 40BO<sub>1.5</sub> · 15GeO<sub>2</sub>). [72]



**Fig. 2.15** SEM microphotographs of crystallized sample  $(45BiO_{1.5} \cdot 40BO_{1.5} \cdot 15GeO_2)$ : (a) prismatic crystals of  $Bi_6B_{10}O_{24}$  and (b) pyramid-shaped crystals of  $Bi_4Ge_3O_{12}$ . [After Nara C.D.S. *et al* [72]]

2.4.2.5 Nanocrystallization of  $SrBi_2Nb_2O_9$  from glasses in the system Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · SrO · Bi<sub>2</sub>O<sub>3</sub> · Nb<sub>2</sub>O<sub>5</sub> [3]

In 2002, Prasad and Varma studied nanocrystallization of SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> from glasses in the system Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · SrO · Bi<sub>2</sub>O<sub>3</sub> · Nb<sub>2</sub>O<sub>5</sub>. XRD patterns obtained for the composition 40(Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) · 60(SrO · Bi<sub>2</sub>O<sub>3</sub> · Nb<sub>2</sub>O<sub>5</sub>) are depicted in Fig. 2.16. Fig. 2.16(a) and (b) showed the XRD patterns recorded at room temperature for the asquenched and 450 °C heat-treated glasses, respectively. These patterns clearly reveal their amorphous nature. Interestingly the samples heat-treated at 500 °C showed peaks of CaF<sub>2</sub> (prototype fluorite) compound (Fig. 2.16(c)). This pattern has fairly broad diffraction peaks, which was attributed to the presence of very fine crystallites of the fluorite phase. Upon further heating at 550 °C, the fluorite phase transformed to the polycrystalline perovskite SBN phase (Fig. 2.16(d)). X-ray peaks corresponding to the oplycrystalline LBO phase were not noticed at this stage of heating. Fig. 2.16(e) showed the XRD pattern recorded for the samples heat-treated at 625 °C. The XRD peaks corresponding to the crystalline LBO phase were not distinguishable in this pattern. However, a slow scan carried out in the 2theta (20) range of 15 to 25° unambiguously suggested the crystallization of the LBO phase (inset of Fig. 2.16(e)).

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Fig. 2.16 XRD patterns of  $40(\text{Li}_2\text{B}_4\text{O}_7) \cdot 60(\text{SrO} \cdot \text{Bi}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5)$  samples: (a) asquenched, heat-treated at (b) 450 °C, (c) 500 °C, (d) 550 °C and (e) 625 °C and slow scan is shown in the inset. [3]

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