CHAPTER 1

Introduction

1.1 Introduction to ferroelectric glass-ceramics

Transparent ferroelectric glass-ceramics (TFGC) is one of glass-ceramic composites. These composites combine the remarkable features of ferroelectric crystals and transparent glass matrix, offering superior ferroelectric non-linear optical (NLO) and electro-optical properties [1]. To fabricate TFGC, the ferroelectric crystal sizes are restricted to a fraction of the light's wavelength (λ_{light}) which should be in nanometer range in order to reduce light-scattering losses, but large enough to retain their ferroelectric effects [1]. To obtain TFGC of silicate based system (SiO_2), the sizes of ferroelectric crystals should be smaller than $\lambda/10$. In such a case where crystallite sizes are in range of $\lambda/10$ to λ, the transparency is reduced causing by large scattering of light, but polarization of incident light is preserved. For translucent to opaque glass-ceramic samples, the crystallites have larger size than λ and the samples become unpolarized [1]. In addition, one of the interesting ferroelectric glass-ceramics, which have different explanation of their transparency behavior, are from tellurite (TeO_2) based glass systems due to their similar refractive indices to that of embedded ferroelectric crystals. This allows the reduction of scattering intensity in large scale [2,3].

The combination of ferroelectric crystals into glass systems has been studied after Stanley Donald Stookey from Corning Glass works [4] had found glass-ceramics in 1950. After that, glass-ceramics have become an interesting subject due to their similar properties to that of polycrystalline materials. To integrate the electrical properties of ferroelectric crystals and the transparency of glass matrix, glass-ceramic method has then been employed. The ferroelectric crystals presented in the glass-ceramics have non-centrosymmetric structure, which leads to non-linear optical properties [1,5-6]. From those advantages, glass-ceramics have the capability to apply in optoelectronic and photonic applications, i.e. electro-optical, high power lasers, optical integrated circuits, adaptive optics, optical resonator, microwave, and pyroelectric devices [6-7]. Many researches have stated that the combination of ferroelectric crystals and glass created interesting properties, such as low light scattering and non-linear property, which is desirable for various applications as mentioned before [1,6-8]. Thus, it is important to perform an insight study for understanding important behaviors of these ferroelectric glass-ceramics.

The ferroelectric material used in this study was potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$ or KNN), which was introduced for the first time in 1960 by Egerton and Dillon [9]. From their report, KNN ceramics were prepared by solid state sintering, which offered many attractive properties especially piezoelectricity. It has been found that the piezoelectric constant (d_{33}) and coupling factor coefficient (k_p) are about 80 pC/N and 0.35, respectively. The increase of temperature caused structural changes. At room temperature, KNN has orthorhombic structure which transforms to tetragonal structure at 200°C. Further increase in temperature than 420°C, tetragonal KNN transforms to cubic structure. In this cubic form, the electrical property of KNN becomes paraelectric which is not appropriate for further electrical applications [10-11]. In 1971, Jaffe et al. [12] found the morphotropic phase boundary (MPB) of KNN which was shown in the of 50 mol% $KNbO_3$: 50 mol% $NaNbO_3$ composition. In this MBP area, the KNN ceramic gained high piezoelectric value, however, this value is still far from that found in lead-based materials (i.e. lead zirconate tianate or PZT). Due to the need of environmental friendly materials to replace the toxic lead-based ceramics, this KNN phase has been subjected to intensive studies as a promising lead-free material.

Normally, it is difficult to produce single phase by using conventional glass-ceramic method [13]. To account for this, the incorporation method has been introduced. This proposing technique provides the fabrication process that reduces the second phase which usually occurred in conventional methods. In this method, the glass batch is prepared from desired single phase compound such as KNN and glass former (SiO_2 or TeO_2), in which single phase as KNN is prepared from calcination method. After that, a batch was melted-quenched and then heat treated at optimized temperature. The successfully preparation of glass-ceramics with single phase was reported for many glass-ceramics systems such as KN-TeO_2 [2], $LiNbO_3$-SiO_2 [13] and also in our previous work with KNN-SiO_2 [14].

Owing to the remarkable optical property in TFGC as NLO or second harmonic generation (SHG) [1,15], many attempts have been made to study the possibility of applying TFGC in optical devices. One of the interesting study is the improvement of low efficiency devices which is able to utilize the energy in range of ultraviolet, UV (10 nm – 400 nm) and infrared (700 nm – 1 mm), i.e. semiconductor solar cell. The semiconductor solar cell absorbs photon in which energy larger than the band gap, while some excess energy always lost by 3 mechanisms; thermalisation process, imperfect collection process and light transmission [16]. This leads to lower solar cell efficiency of about 10 to 20%. Fig. 1.1 shows the AM1.5 terrestrial solar spectrum. From this figure, the vertical lines represent silicon band gaps. It can be seen that the photons in which the wavelength are larger than silicon band gap range are transmitted through the silicon solar cell. Those excess photons are then subjected to create an electron hole-pair per photon, unfortunately it is wasted due to the thermalisation mechanism.

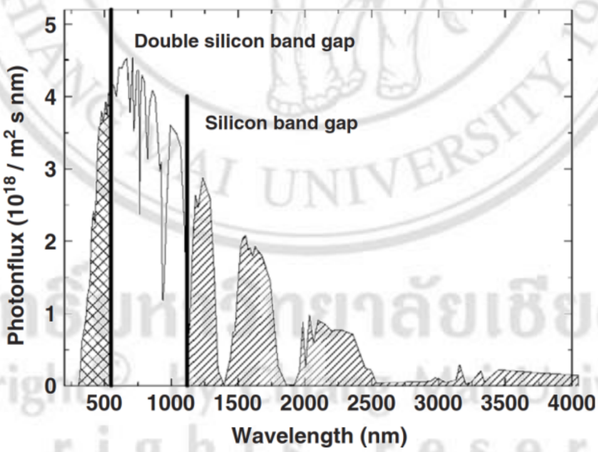

Figure 1.1 AM1.5 terrestrial solar spectrum [16].

To solve those problems, many theoretical hypothesizes has been introduced. The modification of light spectrum is a well research topic. The rare-earth doped materials are used to perform the energy conversion process of light photons to UV or IR photons. Lately, some reports have revealed that rare-earth elements are able to generate the energy states inside band gap, via 3 different processes; up-conversion, down-conversion and photoluminescence. Fig. 1.2 shows simple diagrams which describe the different between those 3 processes.

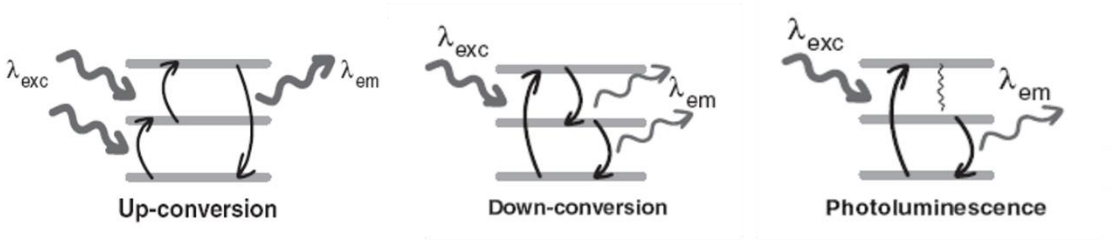

Figure 1.2 Energy conversion process presented by energy level diagrams [16].

Each rare-earth doped material behaves in a particular way. Erbium oxide (Er_2O_3) is one of the rare-earth compounds that show an interesting characteristic [16]. This oxide is the most suitable active ions in several hosts and can generate 3 different energy conversion processes depending on the host. Moreover, its optical transition is in range of 300 nm to near-IR, meaning that energy state of Er_2O_3 matches with f-f transition state. Thus, this attractive characteristic may be helpful for improving device using in wider wavelength. It is also expecting that the advantages of Er_2O_3 can promote the optical behavior of ferroelectric glass-ceramics by modifying the local centers of perovskite structure, leading to an increase in the efficiency of solar energy devices and opto-electronic devices.

In this research, the preparation of $(K_{0.5}Na_{0.5})NbO_3$-TeO_2 and $(K_{0.5}Na_{0.5})NbO_3$-SiO_2 with Er_2O_3 dopant have been carried out. The reason for choosing Er_2O_3 is the compatibility of this rare earth with many host materials [15-17] which is expected to absorb infrared energy for photovoltaic process. The incorporation method was used for preparing the glass-ceramics. The experimental started with the preparation of single phase KNN powder. The well-prepared powder were subsequently mixed with TeO_2 or SiO_2 in a platinum crucible and melted at its melting temperature following by quenching at suitable temperature. The crystallization process of glass-ceramics are accomplished by heat treatment processes. In this thesis, we report the physical feature, thermal behavior, electrical and optical properties of KNN based glass-ceramics in both TeO_2 and SiO_2 system.

1.2 Objectives

1.2.1 To develop glass and glass-ceramic substrates containing ferroelectric potassium sodium niobate (KNN) added erbium oxide.

1.2.2 To study the effects of processing parameters on phase formation, microstructural evolution, electrical and optical properties of the prepared glasses and glass-ceramics.

1.2.3 To find the optimum conditions for producing glass and glass-ceramic substrates for solar cell application.

1.3 Usefulness of the Research

The main education advantages of this work are:

1.3.1 To obtain an understanding of the relevant factors for producing potassium sodium niobate crystals in different base glasses such as TeO_2 and SiO_2 systems with desired physical, microstructural, electrical and optical properties,

1.3.2 To obtain the Er_2O_3 doped potassium sodium niobate based glass and glass-ceramic substrates with desired properties for applications in solar cell and electro-optical devices.