CHAPTER 6

Conclusion and recommended for future works

6.1 General conclusions

In conclusion, potassium sodium niobate (KNN) transparent glasses and glass-ceramics doped erbium oxide were successfully prepared by using incorporation method. In this study, two glass formers of SiO_2 and TeO_2 were selected for comparing the characteristics of each composition. The ferroelectric potassium sodium niobate or KNN crystals inside glass matrix play significant role due to its interesting properties such as non-linear optical and opto-electrical properties. The rare-earth of erbium oxide dopant is expected to improve the optical property of glass and glass-ceramics KNN due to the increasing of structure deformation or so called symmetry changes. This asymmetry can increase the degeneracy in atomic orbitals, which alternately gives the intermediate states inside the energy band gap, leading to the decrease in gap value. The reduction of gap value is caused by the modification of the split in the atomic orbitals relating to the structural deformation and symmetry change. In general glass-ceramic method has been divided into three steps, first step is precursor preparation (via calcination technique); second step is glass forming process (via melting-quenching technique), and final step is crystallization process (via heat treatment technique). The melt-quenching technique has been employed for producing transparent glasses without crystalline phases. The heat treatment process is for the control of growing crystals in size and shape in the glass matrices to obtain glass ceramics in which the crystalline phase as KNN can be precipitated as single or main crystal phase.

6.1.1 KNN-TeO_2 glasses and glass-ceramics and effect of Er_2O_3 dopant

The main conclusion obtained from this study are:

1) Orange glasses and glass-ceramics with composition ratio of 30KNN-70TeO_2 and 20KNN-80TeO_2 showed different characteristics due to compositional fluctuation;

2) It was found that the amount of KNN crystals in glass matrices controlled the thermal stability in producing glasses where the high amount of KNN (30 mol%) promotes the stability of the glass;

3) The increase of the heat treatment temperature of all glass-ceramic conditions promotes an increase in crystal size or increase the volume ratio between the crystal particles and the glass matrix;

4) The XRD results revealed similar crystalline phase of cubic $(K,Na)NbO_3$ in all glass-ceramics with low heat treatment temperature of 300°C–350°C. The glass-ceramics heat treated at T_{c1} and T_{c2} of each glass composition contained additional $Na_2Nb_4O_{11}$, $KNbTeO_6$ and TeO_2 with amount depending on the added KNN content;

5) The maximum dielectric value of about 675 at 10 kHz (low loss of 0.01) was found in 1 mol% Er_2O_3 doped 30KNN-70TeO_2 glass-ceramics which was melted at 900˚C for 30 min and heat treated at 530˚C for 4 h. It can be suggested that high heat treatment temperature is significantly increased the crystallization of KNN solid solution, leading to the increase in dielectric constant;

6) The crystal phases and their sizes in turn play the most important role in controlling physical, appearance, density, dielectric and optical properties of the heat treated glass-ceramics. It was found that the larger amount of KNN (30 mol%) gave the improved properties of the glass-ceramics. And this glass-ceramic posseses high transparency, good mechanical and high dielectric.

6.1.2 KNN-SiO_2 glasses and glass-ceramics and effect of Er_2O_3 dopant

The main conclusion obtained from this study are:

1) In this research, transparent KNN-SiO_2 and Er_2O_3 doped KNN-SiO_2 glasses and glass-ceramics have been successful prepared by incorporation method;

2) It can be found that the heat treatment temperature plays a significant role in controlling the microstructure, crystallite sizes, and crystal quantity of the glass ceramics;

3) Both glass systems offered glasses with pink in color;

4) XRD patterns showed that KNN based glass-ceramics have single phase $K_{0.5}Na_{0.5}NbO_3$ without other precipitation of secondary phase. The Raman spectroscopy found out the peak in region of ~ 850 cm^{-1}, which assigned to vibrations of the Nb-O-Si bond, indicating that probably some niobium ions are inserted in the glass matrix as network formers;

5) The SEM technique revealed the presence of KNN nano-rod crystals inside the glass matrices using the incorporation technique. The crystallite sizes are in range of 50 nm (diameter) and 100-200 nm (longitudinal), and increased with increasing treatment temperatures;

6) For optical property, the as-quenched glass is optically transparent with nearly 80% transmittance in every conditions, and the percent of the transmission was found to continuously decrease with increasing heat treatment temperature due to the growth of KNN crystals;

7) The maximum dielectric constant found in 80KNN-20SiO_2 glass systems was 698 at 10 kHz with a low loss (tanδ) of 0.04 from the sample heat treated at 550°C, however, this sample also had the lowest transparency;

8) It could be observed that the small amount of rare earth Er_2O_3 oxide plays insignificant role in improving the energy state by increasing energy band gap in the KNN-SiO_2 glass-ceramics.

Additionally, the comparison of the important properties of the KNN glass ceramics in this study with other related works are summarized in Table 6.1 (for TeO_2 based glass) and 6.2 (for SiO_2 based glass). It can be seen that glass-ceramics obtained from this research have higher dielectric constant than that reported from other works. Their refractive indices are appreciate for fundamentally optical applications. Furthermore the stability estimated from the thermal profile or so called the possibility of crystallization indicated that glass-ceramics from silicate system are suitable for using in wider temperature range than telluride system. The high energy bang gap of silicate based glass system offers some feasibility of applying this KNN ferroelectric glass-ceramics to alternative power sources, as the top cover of solar cell device for improving the thermalization losses which is the main criterion in reducing the solar cell efficiency.

Table 6.1 Comparison of glass transition temperature (T_g), crystallization temperature (T_c), glass stability factor (ΔT), density (ρ), refractive index (n), energy band gap (Eg) and dielectric constant (ε_r) at various frequency for KNN based tellurite glass system with related works.

Glass system	Er_2O_3 (mol %)	T_g (°C)	T_c (°C)	ΔT (°C)	ρ ($g\text{-}cm^{-3}$)	n	Eg	ε_r (frequency)	Ref
30KNN-70TeO$_2$ [a]		326	420	83	5.14*	2.09*		430 (1kHz)*	♥
20KNN-80TeO$_2$ [a]		350	408	50	4.78*	2.165*	2.40*	470 (1kHz)*	♥
30KNN-70TeO$_2$ [b]	0.5	349	426	67	4.85*	2.06*	3.07*	380 (100kHz)*	♥
30KNN-70TeO$_2$ [b]	1.0	378	432	50	4.84*	2.09*	3.15*	560 (1kHz)*	♥
15K$_2$O-15Nb$_2$O$_5$-70TeO$_2$			495		4.66	2.02		44 (1kHz)	[104]
10Na$_2$O-10Nb$_2$O$_5$-80TeO$_2$		341	390	49	4.93	2.08			[140]
30LiNbO$_3$-70TeO$_2$		360	500	110	4.75	2.11	2.93	32 (100kHz)	[105]
20Nb$_2$O$_5$-80TeO$_2$		421	543	123	5.544	2.10			[86]
10K$_2$O-10Nb$_2$O$_5$-80TeO$_2$		343	496						[88]
10K$_2$O-10Nb$_2$O$_5$-80TeO$_2$	1.0	346	457						[88]
19Na$_2$O-80TeO$_2$	1.0	252			4.83	2.10			[118]

[a] As quenched sample; melted at 800°C for 15min
[b] As quenched sample ; melted at 800°C for 30min
* Annealed sample
♥ This work

Table 6.2 Comparison of glass transition temperature (T_g), crystallization temperature (T_c), glass stability factor (ΔT), density (ρ), refractive index (n), energy band gap (Eg) and dielectric constant (ε_r) at various frequency for KNN based silicate glass system with related works.

Glass system	Er_2O_3 (mol %)	T_g (˚C)	T_c (˚C)	ΔT (˚C)	ρ ($g\text{-}cm^{-3}$)	n	Eg	ε_r (frequency)	Ref
75KNN-25SiO_2		535	645	85	3.61	1.65	4.07	120 (1kHz)♪	♥
80KNN-20SiO_2		520	620	80	3.70	1.65	4.06	20 (1kHz)♫	♥
70KNN-30SiO_2	0.5	579	664	38	3.65*		3.69*	150 (100kHz)*	♥
70KNN-30SiO_2	1.0	563	672	38	3.68*		3.71*	150 (100kHz)*	♥
75KNN-25SiO_2	0.5	558	620	62	3.65*		3.76*		♥
75KNN-25SiO_2	1.0	565	638	57	3.69*		3.77*		♥
80KNN-20SiO_2	0.5	550	601	88	3.78*		3.32*	130 (100kHz)*	♥
80KNN-20SiO_2	1.0	558	607	71	3.74*		2.85*	130 (100kHz)*	♥
70$LiNbO_3$-30SiO_2		575	685		3.834			95 (1kHz)	[141]
13K_2O-10Na_2O-27Nb_2O_5-50SiO_2		660	786	34					[15]
25K_2O-25Nb_2O_5-50SiO_2	0.5	681	759		3.37	1.78		17 (1kHz)	[95]
20K_2O-10Na_2O-25Nb_2O_5-45SiO_2		616	754						[142]

♪ Heat treatment at 525˚C ♫ Heat treatment at 500˚C

* Annealed sample ♥ This work

6.2 Recommendation for future work

In order to increase value of this work, suggestions of future work are given as follows.

- In order to understand about effects of non-linear optical property in these ferroelectric glass-ceramics, the second harmonic generation and the up-conversion should be investigated;
- Other lanthanide or rare-earth ions (such as Yb^{3+}, Tm^{3+}, Ho^{3+} and Eu^{3+}) should be incorporated into KNN glass-ceramics in order to compare properties of KNN glass-ceramics modified with different rare-earth materials;
- KNN with good dielectric and optical properties should be applied as a prototype of glass cover for solar cell device and its efficiency under actual application should be tested.