

## CHAPTER 3

### EXPERIMENT METHODS

#### 3.1 Characterization of zinc waste

In this study zinc waste resulted from zinc refinery process of Padaeng Industry Co., Ltd, Tak province, Thailand has been used as a starting raw material along with other raw materials to produce glasses in suitable compositions. As described previously in Chapter 2 that the compositions of zinc waste generated from different plants can be varied depending on type of zinc minerals and materials adding during zinc recovery process [2, 3], therefore initially, characteristics and properties of zinc waste used in this experiment were investigated by using various techniques as follows:

- Particle size distribution was analyzed by using Master sizer (Malvern, Mastersizer S Ver.2.19) with water as an intermediate solution
- Qualitative and quantitative analysis of chemical compositions were determined by Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Fluorescence Spectroscopy (XRF; Phillips PW-2400)
- Phase formation were examined by X-ray diffractometry (XRD; JEOL JDX-3530)
- Morphology was investigated by Scanning Electron Microscopy (SEM; JEOL JSM-5410)
- Thermal properties were characterized by Thermal Gravimetry and Differential Thermal Analysis (TG-DTA; NETZSCH STA 449C). The temperature condition was set from 30°C to 1400°C with a heating rate of 10°C/min under a flow of air atmosphere.

In addition, phase formation of calcined zinc waste at various temperatures: 300°C, 450°C, 600°C, 800°C, 1150°C and 1300°C were characterized by using XRD

(JEOL JDX-3530) in order to compare the change of phases as the temperature increased.

### 3.2 Experimental design

According to zinc waste contains various kinds of oxide. It is necessary to narrow down to eight particular major oxides which make it easier to study the effect of oxide compositions on glasses and glass-ceramics properties. Eight major oxides, which were  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , have been used to define glass composition experimental region (GCER) as shown in Table 3.1. Twenty-five different glass compositions were designed by using Mixsoft Computer software based on a mixture experiment [25]. The composition regions were defined by lower and upper bounds on the components. These composition regions were selected from preliminary study.

Table 3.1 Compositional constraints for experimental design (%wt)

Single-component constraints Lower and upper bound	Multiple-component constraints Lower and upper bound
$45 < \text{SiO}_2 < 65$	$\text{CaO} + \text{Na}_2\text{O} > 20$
$5 < \text{B}_2\text{O}_3 < 15$	$\text{SiO}_2 + \text{B}_2\text{O}_3 > 60$
$10 < \text{CaO} < 20$	
$0 < \text{MgO} < 10$	
$1 < \text{ZnO} < 3$	
$1 < \text{Al}_2\text{O}_3 < 5$	
$3 < \text{Fe}_2\text{O}_3 < 5$	

The upper and lower bounds for each major oxide were selected based on the principles of glass formulation and glass properties. The multiple-component bounds were defined for network modifier oxides ( $\text{CaO} + \text{Na}_2\text{O}$ ) and network former oxides ( $\text{SiO}_2 + \text{B}_2\text{O}_3$ ). These bounds offer the opportunity to explore compositional regions that could form glasses with acceptable properties. Oxide compositions in each glass composition resulting from the design of Mixsoft-software are shown in Table 3.2. The oxide

compositions of glass composition number 13 and 14 are identically controlled to examine reproducibility of the experimental design.

Table 3.2 Suitable percent of oxides of 25 glass compositions (%wt)

GC#	Composition (%wt)							
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	MgO	ZnO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
1	45.00	15.00	15.00	20.00	0.00	1.00	1.00	3.00
2	55.00	5.00	15.00	10.00	10.00	1.00	1.00	3.00
3	45.00	15.00	11.00	10.00	10.00	1.00	5.00	3.00
4	45.00	15.00	11.00	20.00	0.00	1.00	5.00	3.00
5	45.00	15.00	5.00	18.00	10.00	3.00	1.00	3.00
6	45.00	15.00	11.00	10.00	10.00	3.00	1.00	5.00
7	63.00	5.00	15.00	10.00	0.00	3.00	1.00	3.00
8	59.00	5.00	15.00	10.00	0.00	3.00	5.00	3.00
9	47.00	15.00	15.00	10.00	0.00	3.00	5.00	5.00
10	57.00	5.00	5.00	20.00	0.00	3.00	5.00	5.00
11	45.00	15.00	13.00	20.00	0.00	3.00	1.00	3.00
12	47.00	15.00	5.00	20.00	0.00	3.00	5.00	5.00
13	60.00	15.00	5.00	15.00	0.00	1.00	1.00	3.00
14	60.00	15.00	5.00	15.00	0.00	1.00	1.00	3.00
15	64.00	5.00	5.00	15.00	0.00	1.00	5.00	5.00
16	58.00	15.00	10.00	10.00	0.00	1.00	1.00	5.00
17	56.00	5.00	5.00	15.00	10.00	1.00	5.00	3.00
18	45.00	15.00	10.00	10.00	9.00	1.00	5.00	5.00
19	64.00	5.00	10.00	10.00	0.00	3.00	5.00	3.00
20	56.00	15.00	10.00	10.00	0.00	3.00	1.00	5.00
21	56.00	5.00	5.00	15.00	10.00	3.00	1.00	5.00
22	55.00	5.00	15.00	10.00	8.00	1.00	1.00	5.00
23	55.00	5.00	15.00	18.00	0.00	1.00	1.00	5.00
24	55.00	5.00	13.00	20.00	0.00	1.00	1.00	5.00
25	55.00	5.00	5.00	20.00	8.00	3.00	1.00	3.00

Note that  $B_2O_3$  was added in glass compositions to obtain alkaline and alkaline earth borosilicate glass. These glasses give high chemical durability that can reduce the leachability of Pb from glass-ceramic products.

Due to eight major oxides have been defined by the lower and upper bounds, thus the lower bound and upper bound are considered as the minimum and maximum weight percent of each major oxide required for producing glasses. Consider oxide compositions of the designed 25 glass compositions in Table 3.2 and oxide compositions contain in zinc waste analyzed by XRF (100% waste) in Table 3.3. It was found that zinc waste contains un-suitable percent of oxide compositions to producing glasses by itself due to the lack of  $SiO_2$ ,  $B_2O_3$ ,  $Na_2O$  (less than lower bound) and the excess of  $ZnO$ ,  $Al_2O_3$  and  $Fe_2O_3$  (more than upper bound).

Table 3.3 Calculation of suitable percent of zinc waste as raw material

Oxides	Lower - upper bound	100% waste (XRF)	30% waste
$SiO_2$	45 - 65	22.66	6.80
$B_2O_3$	5 - 15	0.00	0.00
$Na_2O$	5 - 15	0.63	0.19
$CaO$	10 - 20	16.43	4.93
$MgO$	0 - 10	0.29	0.09
$ZnO$	1 - 3	3.09	0.93
$Al_2O_3$	1 - 3	3.67	1.10
$Fe_2O_3$	3 - 5	7.32	2.20

The problems have been solved by reducing percent of zinc waste and adding other raw materials. Reducing percent of zinc waste to 30% causes the lower percents of  $ZnO$ ,  $Al_2O_3$  and  $Fe_2O_3$  fit into the region of their lower and upper bounds. As a result the rest of oxides, which were  $SiO_2$ ,  $B_2O_3$ ,  $Na_2O$ ,  $CaO$ ,  $MgO$  and  $Fe_2O_3$ , need to be added to reach the suitable percent of oxides in each glass follow Table 3.2 as described in Appendix A.

Table 3.4 Eight raw materials used as sources of added-oxides (%wt)

GC#1	Silica sand (SiO <sub>2</sub> )	Boric acid (B <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O)	Soda ash (Na <sub>2</sub> CO <sub>3</sub> )	Limestone (CaCO <sub>3</sub> )	MgCO <sub>3</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
1	38.20	26.57	25.32	26.91	0.00	0.07	0.00	0.80
2	48.20	8.86	25.32	9.05	20.81	0.07	0.00	0.80
3	38.20	26.57	18.48	9.05	20.81	0.07	3.90	0.80
4	38.20	26.57	18.48	26.91	0.00	0.07	3.90	0.80
5	38.20	26.57	8.22	23.34	20.81	2.07	0.00	0.80
6	38.20	26.57	18.48	9.05	20.81	2.07	0.00	2.80
7	56.20	8.86	25.32	9.05	0.00	2.07	0.00	0.80
8	52.20	8.86	25.32	9.05	0.00	2.07	0.00	0.80
9	40.20	26.57	25.32	9.05	0.00	2.07	3.90	2.80
10	50.20	8.86	8.22	26.91	0.00	2.07	3.90	2.80
11	38.20	26.57	21.90	26.91	0.00	2.07	0.00	0.80
12	40.20	26.57	8.22	26.91	0.00	2.07	3.90	2.80
13	53.20	26.57	8.22	17.98	0.00	0.07	0.00	0.80
14	53.20	26.57	8.22	17.98	0.00	0.07	0.00	0.80
15	57.20	8.86	8.22	17.98	0.00	0.07	3.90	2.80
16	51.20	26.57	16.77	9.05	0.00	0.07	0.00	2.80
17	49.20	8.86	8.22	17.98	20.81	0.07	3.9	0.80
18	38.20	26.57	16.77	9.05	18.71	0.07	3.9	2.80
19	57.20	8.86	16.77	9.05	0.00	2.07	3.9	0.80
20	49.20	26.57	16.77	9.05	0.00	2.07	0.00	2.80
21	49.20	8.86	8.22	17.98	20.81	2.07	0.00	2.80
22	48.20	8.86	25.32	9.05	16.61	0.07	0.00	2.80
23	48.20	8.86	25.32	23.34	0.00	0.07	0.00	2.80
24	48.20	8.86	21.90	26.90	0.00	0.07	0.00	2.80
25	48.20	8.86	8.22	8.59	16.61	2.07	0.00	0.80

### 3.3 Preparation of glasses

The Zinc waste and other raw materials were crushed and ground then sieved through a sieve #100 mesh to make the particle size small and easy to be dissolved during melting process. Moisture in zinc waste and raw materials was decomposed by drying in the oven at 60°C for one hour. In each glass composition thirty percent of zinc waste was weighted and mixed with other raw materials follows the ratios in Table 3.4. The mixture was loaded into ceramic crucible (alumina-zircon) and melted in a glass melting furnace as shown in Fig. 3.1 at 1450°C for one hour. The melted glass was then poured on a pre-heated stainless steel mold (~300°C) to avoid the thermal shock and was left to cooling down in the air.

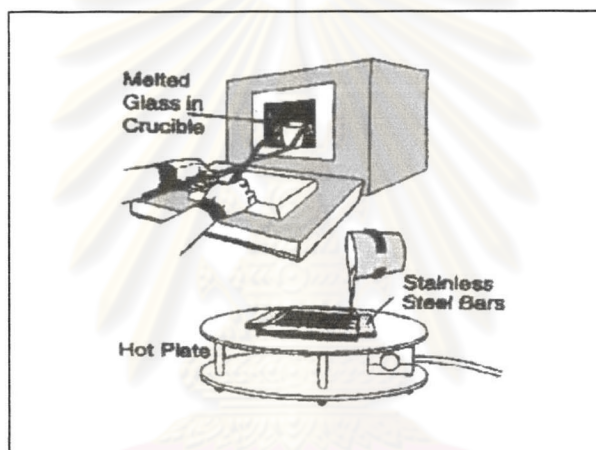


Fig. 3.1 Glass melting process

### 3.4 Characterization of melted glasses

#### 3.4.1. Physical behavior

The twenty-five melted glasses were investigated their melting behavior (viscosity), melted-homogeneity, color and phase separation by visual observation and optical microscopy (OM; Olympus BX 60MF5).

### 3.4.2. Thermal behavior

In order to study crystallization behavior, Differential Thermal Analysis experiments (DTA; Netzch STA 449C) were performed to determine the approximate glass transition temperature,  $T_g$  and crystallization temperature,  $T_c$  of each glass sample. The analyzer measured the difference between the sample thermocouple and the reference ( $\text{Al}_2\text{O}_3$ ) thermocouple with respect to the temperature of the furnace. A 30 mg sample of glass powder was loaded into an alumina crucible. Glass and reference were heated from  $30^\circ\text{C}$  to  $1200^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  under a flow of air atmosphere.

## 3.5 Preparation of glass-ceramics

Preparation of glass-ceramic specimens was performed by heat-treatment process. The temperatures used in heat-treatment process were designed by using glass transition temperature,  $T_g$  and crystallization temperature,  $T_c$  as a guideline. It is noted that the specimens were made from glass powder.

### 3.5.1. Preparation of glass-ceramic specimens

Each melted glass was crushed and ground to fine powder then sieved through sieve #100. To make the powder pack easily together, polyvinyl alcohol (PVA) was mixed with 5 grams of glass powders by hand. Then the mixture was pressed to form glass pellets using a uni-axial pressing machine with a 10 KN load.

### 3.5.2. Heat treatment process

Heat treatment process of producing glass-ceramics including two main steps: nucleation and crystal growth. Firstly, the samples were heat-treated up to nucleation temperature and hold at this temperature for 1 hour, and then further heat-treated up to crystal growth temperature and hold at this temperature for 2 hours. The nucleation and crystal growth temperatures were varied in four conditions as shown in Table 3.5 by fixing the nucleation and crystal growth time at 1 and 2 hours, respectively.

Table 3.5 Conditions of heat treatment process

Conditions	Heat treatment process	
	Nucleation ( °C)	Crystal growth ( °C)
	1 hour	2 hours
A	550	650
B	650	750
C	750	850
D	850	950

### 3.6 Characterizations of glass ceramics

#### 3.6.1. Physical properties

##### - Volume shrinkage behavior

Volume shrinkage of glass-ceramic samples condition A, B, C and D was calculated by measuring the dimension before ( $V_B$ ) and after ( $V_A$ ) heat treatment. The volume shrinkage was calculated as follows:

$$\text{Volume shrinkage (\%)} = \left[ \frac{(V_B - V_A)}{V_B} \right] \times 100 \quad (\text{eq.3.1})$$

##### - Water absorption, apparent porosity, bulk density and apparent density

Percent of water absorption ( $W.A$ ), percent of apparent porosity ( $A.P$ ), bulk density ( $B.D$ ), and apparent density ( $A.D$ ) of glass-ceramic samples condition A, B, C and D were determined by using Archimedes' method. The equations for calculation are shown as follows:

$$W.A = \left[ \frac{(W_3 - W_1)}{W_1} \right] \times 100 \quad (\text{eq. 3.2})$$

$$A.P = \left[ \frac{(W_3 - W_1)}{(W_3 - W_2)} \right] \times 100 \quad (\text{eq. 3.3})$$



$$B.D = \left[ \frac{W_1}{(W_3 - W_2)} \right] \times \text{Density of water} \quad (\text{eq. 3.4})$$

$$A.D = \left[ \frac{W_1}{(W_1 - W_2)} \right] \times \text{Density of water} \quad (\text{eq. 3.5})$$

Where,  $W_1$  is dry weight (g)

$W_2$  is weight in water (g)

$W_3$  is water filled weight (g)

### 3.6.2. Crystal phase formation

Crystalline phase formed of twenty-five heat-treated glasses (glass-ceramics) at condition B and C were identified by using X-ray diffractometry (XRD; Bruker D8 Advance) to investigate the development of phases as the heat-treatment temperature increases. The data was collected using a copper X-ray source (CuK $\alpha$ ). Glass-ceramic powder ~100 mg was loaded in sample holders and placed on the stage. Condition B; the scan was performed from  $10^\circ \leq 2\theta \leq 70^\circ$  by using a step of 0.04 $^\circ$ /sec at room temperature. Condition C; the scan was performed from  $10^\circ \leq 2\theta \leq 70^\circ$  by using a step of 0.02 $^\circ$ /sec at room temperature.

### 3.6.3. Crystal morphology

Morphology, size and distribution of crystals formed in glass-ceramic specimens at condition B and C were characterized by using Optical Microscope (OM; Olympus BX 60MF5) and Scanning Electron Microscope (SEM; JEOL JSM6301F). Twelve selected samples, which are GC#2, GC#3, GC#4, GC#5, GC#8, GC#10, GC#13, GC#14, GC#19, GC#23, GC#24, GC#25, were cut in cross-section and mounted in resin then polished by using SiC paper started from #400, #800 and down to #1200. Finally the samples were polished by diamond paste 1  $\mu\text{m}$  to obtain the flat mirror like surface. The compositions of crystals and glass matrix formed in glass-ceramics were examined by Electron Dispersive Spectroscopy (EDS).

#### 3.6.4. Mechanical property

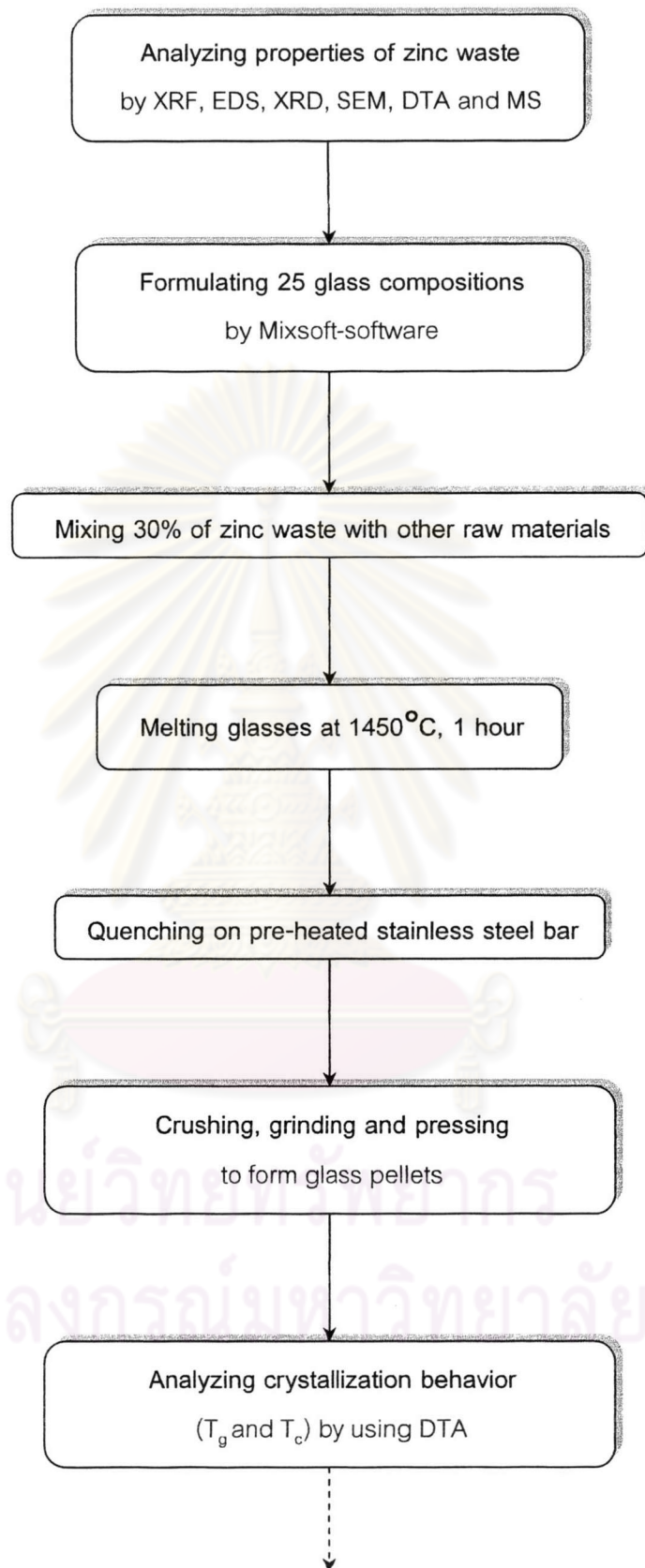
Mechanical strength of the glass-ceramic samples was measured by three point bending method. Prior to the heat treatment, samples were prepared by pressing glass powder as a rectangular bar of 0.5 x 1.0 x 5.0 cm in dimension. The sample bars were heat-treated in condition B and C with respect to Table 3.5 Then they were polished by using SiC powder particle size less than 2000 mesh on front and back surfaces until the surfaces smooth and flat like a mirror. Five bars were prepared for each glass-ceramic sample. All tests were performed using LLOYD 500, Intro enterprise Co., Ltd. The crosshead speed was constant at 0.5 mm/min.

#### 3.6.5. Chemical durability

To evaluate the release of the hazardous elements in the glass-ceramics samples, the standard toxic characterization leaching procedure (TCLP) was carried out following method 1311 [26]. It is noted that TCLP method used in this study has been adjusted from the original one. The size of sample powder was reduced if the surface area was out of the limits stated in a standard procedure. A one hundred gram sample was mixed in an appropriate extraction fluid, transferred in a covered beaker, stirred at ambient temperature at medium rpm for 20 hours. The liquid was separated by filtration and analyzed to determine the amount of toxic metal of interest (Pb in this experiment) by atomic absorption spectrometry (AAS).

#### 3.6.6. Coefficient of thermal expansion

Coefficient of thermal expansion of glass-ceramic samples condition C was obtained for all samples using dilatometer (DIL 402C). Glass ceramics samples were cut as a rectangular bar of 5 x 5 x 8 mm. The temperature condition was set from 100°C to 400°C with a heating rate of 10°C/min. It is noted that different temperature ranges were used to determine the thermal expansion coefficient by considering only the range of graph between  $dL/dL_0\%$  and temperature that shows straight slope



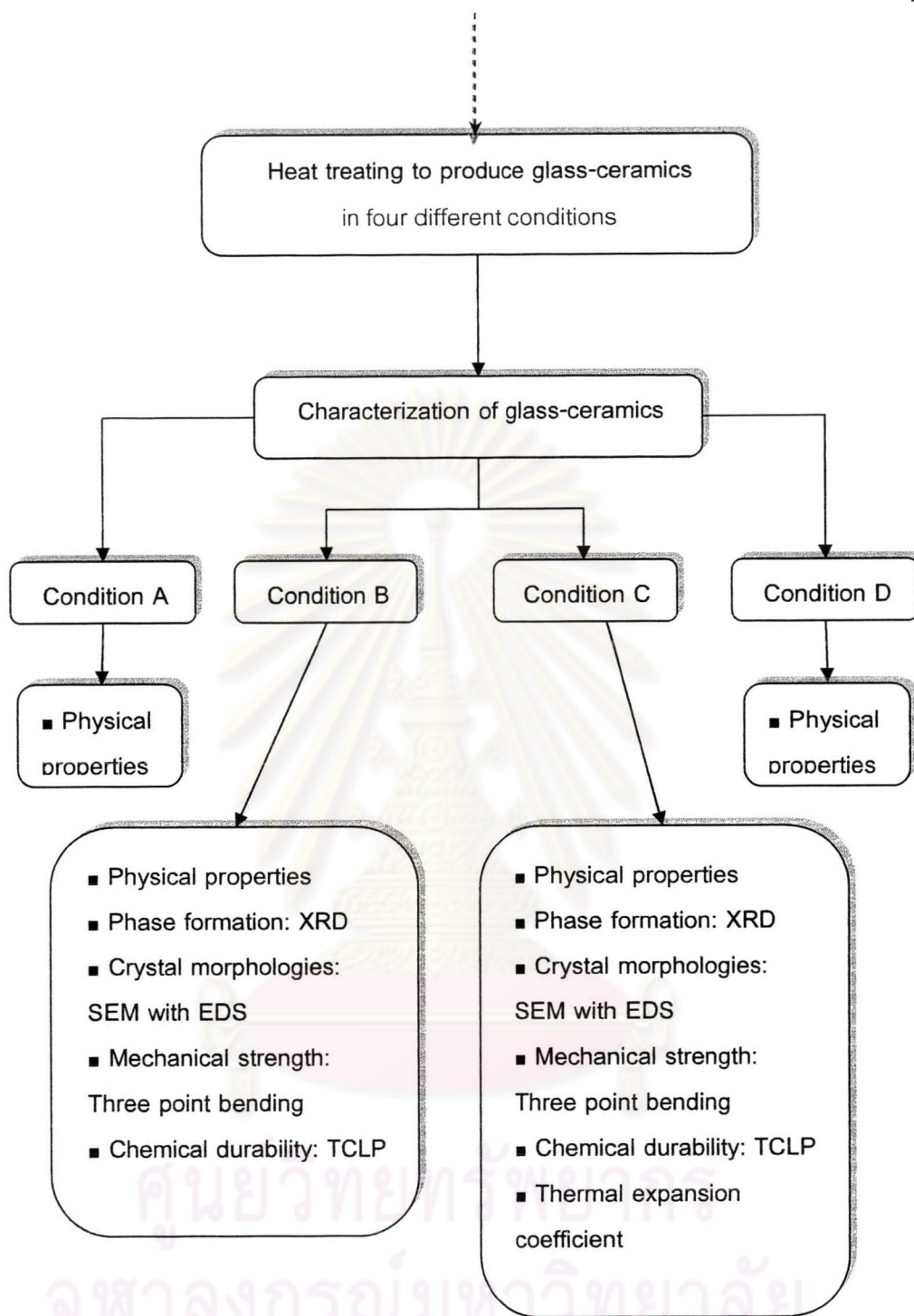


Fig.3.2 Flow chart of the experiment methods