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Article

Effect of Alkaline and Alkaline-Earth Metal Oxides Addition on the Glass Formation and Crystallization of ZnO-Al$_2$O$_3$-SiO$_2$ Glasses

Panitpicha Yaowakulpattana[a], Takashi Wakasugi[b], Shinya Kondo, and Kohei Kadono

Kyoto Institute of Technology, Hashigami-chou, Matsugasaki, Kyoto, Japan 606-8585
E-mail: [a]y.panitpicha@gmail.com, [b]waka@kit.ac.jp (Corresponding author)

Abstract. The effect of alkaline and alkaline-earth metal oxides addition to the ZnO-Al$_2$O$_3$-SiO$_2$ system on the glass formation has been studied and the crystallization behaviour of these glasses was investigated by DTA and XRD. The addition of alkaline metal oxides tends to hinder the glass formation and only the system containing Li$_2$O forms glass. The addition of Li$_2$O changes the crystallization behaviour and the precipitation of LiAlSi$_3$O$_8$ is caused together with gahnite which is a typical precipitation phase in the ZnO-Al$_2$O$_3$-SiO$_2$ system. TiO$_2$ added as a nucleating agent tends to form a compound with ZnO when extra ZnO exists. All glasses could be formed when alkaline-earth metal oxides were added and the colour was changed to be brown by the addition of TiO$_2$. In case of no TiO$_2$ addition, glasses changed the form and melted before finish DTA because of low viscosity or high nucleation rate. However, crystallization peaks were clearer after added TiO$_2$ due to the effect of nucleating agent. To conclusion, some glasses could not be formed when alkaline metal oxide was added because crystal growth rate was higher than alkaline-earth metal oxide addition; however, transparent glasses could not be obtained in all samples.

Keywords: Transparent glass-ceramics, nucleating agent, gahnite, crystallization.

1. Introduction

Transparent glass-ceramics are attractive materials as optical advices because they have both the good formability of glasses and excellent optical properties of crystals. The size of crystals in transparent glass-ceramics must be smaller than the wavelength of visible light to reduce the scattering of light at the interface of crystals. For this purpose, glasses showing volume crystallization are desired because the growth of crystals is hindered by the other crystals around them so that the size of crystals can be controlled by the number density of nuclei. In addition, some nucleating agents (such as TiO_2, ZrO_2, P_2O_5, Cr_2O_3, etc.) are required to increase the number density of nuclei. One of the authors researched about the nucleation behaviour of Na_2O-SiO_2 glass with 2 mol% of ZrO_2 as a nucleating agent and found the shift of Tc to higher temperature because of the increase of viscosity by the addition of ZrO_2 [1]. Rezvami investigated the effects of Cr_2O_3, Fe_2O_3, and TiO_2 as nucleating agents on the crystallization behaviour of SiO_2-Al_2O_3-CaO-MgO (R_2O) glass by DTA, XRD, and SEM [2]. They found that TiO_2 and Fe_2O_3 with 3 wt% of Cr_2O_3 prevent the phase separation and the crystallization in glass specimens. Morimoto and Kuriyama reported that the addition of more than 5 wt% of TiO_2 with small amount of R_2O+RO leads to phase-separation because ionic radius of Ti^{4+} is larger than Si^{4+} [3]. At lower temperatures than glass transition temperature (T_g), Ti^{4+} prefers octahedral or cubic coordination. On the other hand, Ti^{4+} was four-fold coordinated at higher temperatures than T_g. In addition, Ti^{4+} becomes six-fold coordination as nucleation occurred. Tammann et al reported that if the viscosity at T_m is higher, the crystallization ability becomes lower [4].

Moreover, the relationships of T_g and temperatures with maximum nucleation rate (T_{max}) or crystal growth rate (U_{max}) has been studied in many publications. Fokin et al plotted the maximum crystal growth rate (U_{max}) versus reduced glass transition, T_{gr} ($=T_g/T_m$ where T_m is melting temperature) for 20 Silicate glasses and confirmed the hypothesis the maximum nucleation rate (I_{max}) decreased with T_{gr} [5, 6]. And they compared U_{max} with theoretical predictions [7]. As the results, U_{max} dropped with increase of T_{gr} because of the increased of viscosity at T_{max}, together with the decrease in thermodynamic driving force. In addition, these results are good correlation between theory and experiment, and also show that the screw dislocation growth model is a good estimation to describe crystal growth in silicate glass. They also researched about the relationships between I_{max} and T_{gr} of glass-forming liquids [8]. They concluded that the increase of T_{gr} leads to decrease in I_{max} or increase of T_{max} which are correlated with calculations and experimental data. Differential thermal analysis (DTA) is used widely to investigate crystallization behaviour of glasses [9-12]. There are three main characteristics of DTA curves: first is small endothermic peak corresponds to T_g, second is sharp exothermic peaks represents for crystallization peak temperature (T_c) of glass, and last is broad endothermic peak at high temperature due to the formation of liquid phase.

Gupta et al studied primary crystallization behaviour of K_2O-SiO_2-LiF-MgF_2-MgO glasses with and without 1.2 wt% of CaF_2 addition by DTA, SEM, and XRD [13]. Their results showed that initial of T_c shifted to lower temperature because of the increase of number of nuclei and later shifted to higher temperature because crystal grows during DTA. Wakasugi et al presented that pre-DTA heat-treatment should be carried out at low enough temperature where only nucleation occur [1].

The effect of crystal sizes on crystallization temperature has also been researched. Fokin et al researched about the dependence of crystal/liquid surface energy on the temperature and size for two Silicate glasses ($Li_2O.2SiO_2$ and $Na_2O.2CaO.3SiO_2$) by using Tolman's equation to calculate size dependent surface tension [14]. As a result, surface energy decreases with temperature and the increase of surface energy is caused by the change of crystal size. The value of temperature dependence on surface energy is close to theoretical predictions; therefore, Tolman parameter was chosen. Cabral reported on the critical cooling rate (q_{cr}) of seven Silicate Glass samples [15]. The results showed that T_c varied about 50 - 60°C with the change of cooling rate of 10 - 20°C/min. Moreover, the materials of crucible (such as Pt, C, and Al_2O_3) also affected to T_c.

As we know that main component for glass production is SiO_2 which acts as glass former; therefore, they were used in many glass systems. Here are some examples; Roskosz et al investigated nucleation and crystal growth in CAS (CaO-Al_2O_3-SiO_2) system which is a good choice because glass-forming region is wide [16]. It is true that the mobility of network-modifying cation controls the composition and structure of nucleating phases which implies that viscosity controlled by network formers is not an important parameter for nucleation. Wittman et al studied on surface nucleation and growth of Anorthite ($CaO.Al_2O_3.2SiO_2$) glass [17]. The results showed that surface nucleation occurs and the crystal grew towards the centre. This indicated that the interfacial rearrangements controls crystal growth of isolated

crystal on the surface but the long-range diffusion is not the main subject in this study. Patridge et al reported that the surface crystallization of ZAS glasses was hindered by the ambient vapour which does not contain O_2 or H_2O [18]. Ray and Day measured the q_{cr} for five compositions in the $BaO-TiO_2-SiO_2$ system and presented that the tendency for glass formation increases with the increase of Silica content [19]. Potapov reported that adding Na_2O less than 30% instead of Li_2O in Lithium Disilicate (LS_2) affected the nucleation rate to decrease without affecting the crystal growth [20].

Preparation of transparent glass ceramics was reported for various systems. Pinckney introduced K_2O about 10 - 20 wt% to the $ZnO-Al_2O_3-SiO_2$ (ZAS) system and highly transparent glass ceramics with crystallinity about 10 - 25% were obtained, in which small ZnO crystals of 5 - 20 nm precipitated [21]. However, samples became translucent when crystallinity was greater than 25%. Hou et al. showed that in ZAS system with 3 wt% of Li_2O, 5 wt% of TiO_2, and 0.5 wt% of Sb_2O_3, transparent glass ceramics containing gahnite as a major phase were obtained [22]. It is mentioned that quartz became the main phase after the heat-treatment at higher than 1100°C, and samples lost their transparency because of the scattering at the interface of SiO_2 crystals.

Since high temperature is required to melt ZAS glasses (> 1550 °C) [23], it is desired to lower the processing temperature by using some additives as a flux. In this paper, the effect of alkaline and alkaline-earth metal oxides on the glass formation for $ZnO–Al_2O_3–SiO_2$ glasses with TiO_2 as nucleating agent were investigated, and the effect on crystallization mechanism was discussed.

2. Experimental Procedures

The chemical compositions of samples with adding alkaline and alkaline-earth metal oxides were given in Table 1 and Table 2, respectively. $20ZnO·20Al_2O_3·60SiO_2$ (mol%) was chosen as the base glass (20AZ). TiO_2 was introduced as a nucleating agent. Alkaline metal oxides (such as Li_2O, Na_2O, and K_2O) and alkali-earth metal oxides (CaO, SrO, BaO) were added as fluxing agents.

Table 1. Glass compositions (mol%).

	ZnO	Al_2O_3	SiO_2	Li_2O	Na_2O	K_2O	TiO_2
20AZ	20	20	60	-	-	-	-
20AZ3Li	20	20	57	3	-	-	-
20AZ3Na	20	20	57	-	3	-	-
20AZ3K	20	20	57	-	-	3	-
20AZ6T	20	20	54	-	-	-	6
20AZ3Li6T	20	20	51	3	-	-	6
20AZ3Na6T	20	20	51	-	3	-	6
20AZ3K6T	20	20	51	-	-	3	6

Table 2. Glass compositions (mol%).

	ZnO	Al_2O_3	SiO_2	CaO	SrO	BaO	TiO_2
20AZ3Ca	20	20	57	3	-	-	-
20AZ3Sr	20	20	57	-	3	-	-
20AZ3Ba	20	20	57	-	-	3	-
20AZ3Ca6T	20	20	51	3	-	-	6
20AZ3Sr6T	20	20	51	-	3	-	6
20AZ3Ba6T	20	20	51	-	-	3	6

Batches with given compositions were mixed well and melted in a platinum crucible at 1600°C for 2 hours. Afterwards, the melts were casted in a carbon mould and cooled rapidly to the room temperature. Casted samples were kept at temperature (675°C -825°C) for nucleation heat-treatment (NHT) for 24 hours, and their crystallization behaviour was studied by DTA instrument (Rigaku Thermo Plus TG 8120) with a

heating rate of 10°C/min to 1200°C, using Al_2O_3 powder as reference material in order to investigate the T_g and T_c of them. Crystalline phases in the sample after crystallization were identified by X-ray diffraction (XRD) analysis (Rigaku RINT-2500V) using CuKα radiation with operating power 40 kV, 200 mA. The full width at half maximum (FHWM) peak of XRD was used to calculate crystal sizes by Scherrer's equation.

3. Results and Discussion

The appearances of as-casted samples are shown in Table 3 and 4. According to Table 3, only 20AZ3Li and 20AZ3Li6T became glasses among samples containing alkaline metal oxides, and the others crystallized and became opaque. 20AZ3Li6T crystallized partially by surface crystallization and its glassy part had light yellow colour which is also shown in other glasses containing TiO_2. This color is estimated to be caused by Ti^{3+} produced during melting [24]. According to Table 4, all samples containing alkaline-earth metal oxides did not crystallized and became glasses. Indeed, the decrease of viscosity by the addition of alkaline-earth metal oxides is smaller than alkaline metal oxides. In this case, addition of alkaline metal oxides (such as Na_2O, K_2O) accelerated the crystal growth rate to be higher than alkaline-earth metal oxides; therefore, glasses could not be formed.

Table 3. Appearances of as-casted glasses in case of the alkaline metal oxide addition.

Code	20AZ	20AZ3Li	20AZ3Na	20AZ3K
Appearance				

Code	20AZ6T	20AZ3Li6T	20AZ3Na6T	20AZ3K6T
Appearance				

Table 4. Appearances of as-casted glasses in case of the alkaline-earth metal oxide addition.

Code	20AZ3Ca	20AZ3Sr	20AZ3Ba
Appearance			

Code	20AZ3Ca6T	20AZ3Sr6T	20AZ3Ba6T
Appearance			

Figure 1 shows crystalline phases of as-casted samples which did not become glasses. In every sample, gahnite precipitated. Among alkaline metal oxides, generally, Li_2O is the least effective to decrease the viscosity of glass melts. Therefore, the increase of crystal growth rate by the decrease of viscosity would be a reason why glass was not obtained for the samples containing Na_2O or K_2O.
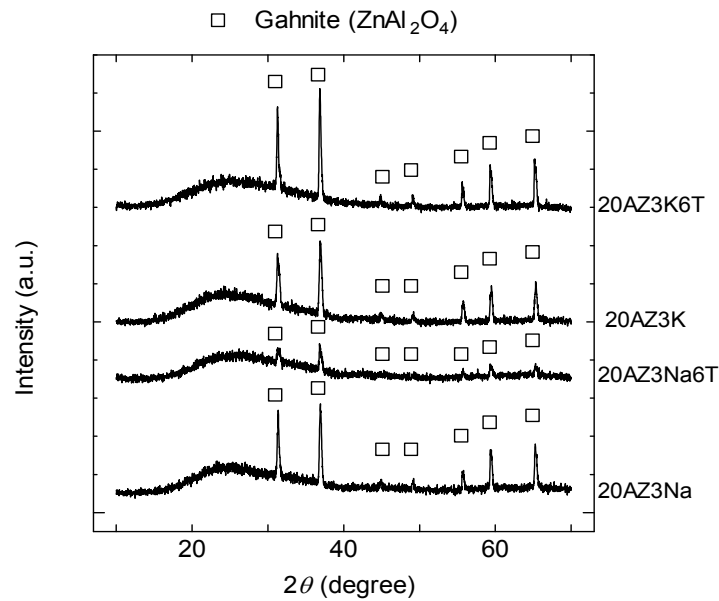
Fig. 1. XRD patterns of as-casted samples before DTA of 20AZ3Na, 20AZ3Na6T, 20AZ3K, and 20AZ3K6T, respectively.

Crystallization behaviours of base glass samples, for which various NHT was performed, were studied by DTA apparatus. It is reported that the nucleation of gahnite proceeds during NHT. [25] The XRD patterns of samples after DTA are shown in Fig. 2. Precipitation of gahnite ($ZnAl_2O_4$) and quartz (SiO_2) was observed. The intensity of quartz depends on the NHT temperature because the increase of nuclei promotes the precipitation of gahnite, which hinders the precipitation of quartz and becomes vigorous at higher than 750ºC. The increase of nucleation rate of gahnite at these temperatures would be a reason of this behaviour. Crystalline phases precipitated in heat-treated 20AZ3Li and 20AZ3Li6T during DTA were shown in Fig. 3 and 4, respectively. Introduction of Li_2O into the system caused the precipitation of lithium aluminium silicate ($LiAlSi_3O_8$) as a main phase instead of gahnite. No precipitation of such alkaline aluminosilicate phase was observed when Na_2O or K_2O was added, and it was found that introducing small amount of Li_2O has much effective on the crystallization process. A split of crystallization peak was observed for 20AZ3Li in DTA measurement though 20AZ showed a single peak. This also means the change of crystallization behaviour by the addition of Li_2O. In this system, $ZnTiO_3$ and willemite ($ZnSiO_4$) also precipitated as minor phases.
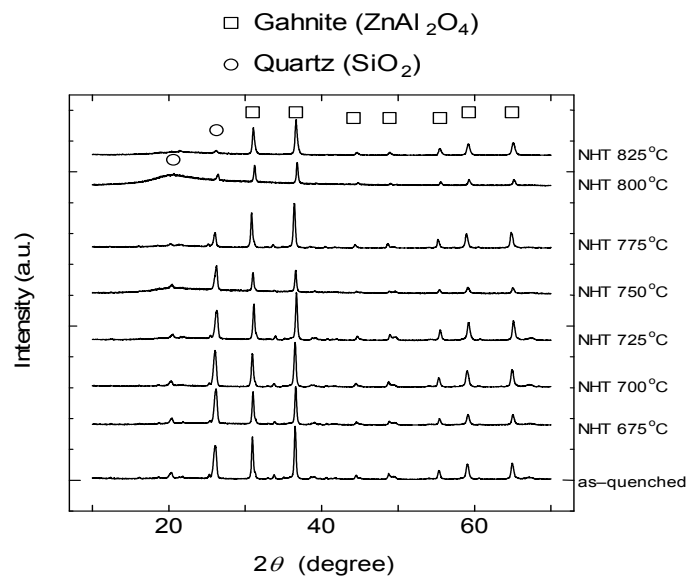

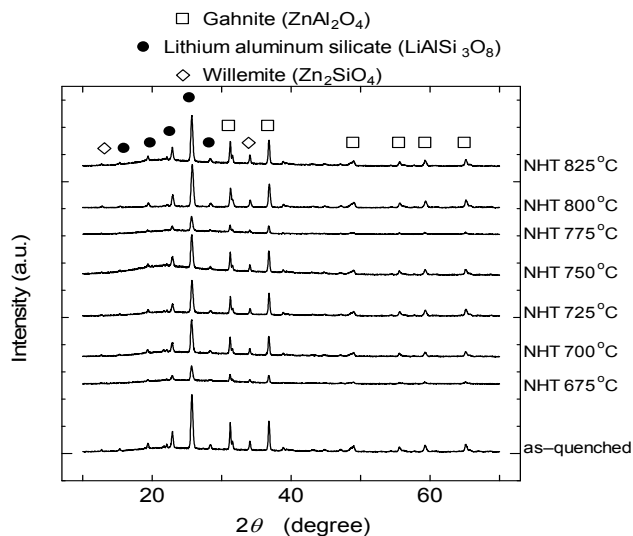Fig. 2. XRD patterns of 20AZ at various NHT temperatures.

Fig. 3. XRD patterns of 20AZ3Li at various NHT temperatures.
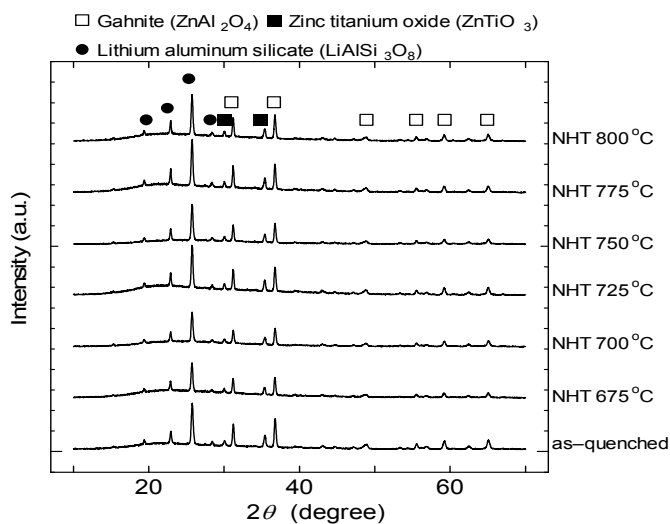

Fig. 4. XRD patterns of 20AZ3Li6T at various NHT temperatures.
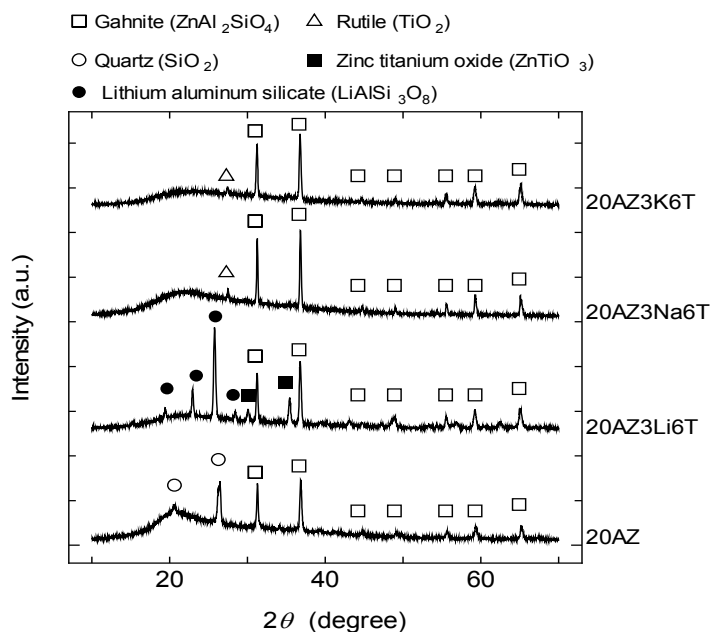

Fig. 5. XRD patterns of 20AZ, 20AZ3Li6T, 20AZ3Na6T, and 20AZ3K6T, respectively.

The effect of adding alkaline metal oxides with nucleating agent on the crystalline phases was shown in Fig. 5. Lithium aluminium silicate is the predominant phase when Li_2O was added. Gahnite and zinc titanium oxide were minor phases in 20AZ3Li6T; meanwhile, Rutile precipitated as a minor phases in 20AZ3Na6T and 20AZ3K6T. That means ZnO remains much in glassy phase so all TiO_2 combine with ZnO to be $ZnTiO_3$ in 20AZ3Li6T. On the other hand, in 20AZ3K6T and 20AZ3N6T, ZnO is consumed for the precipitation of Gahnite and there are lacks of ZnO in glassy phase. Therefore, the rest of ZnO in glass combines with TiO_2 to be $ZnTiO_3$ and the rest of TiO_2 precipitated independently as rutile. In order to investigate the crystallization process of 20AZ3Li, precipitated phases in samples which were heated to selected temperatures (800°C, 900°C, 1000°C, 1100°C, and 1200°C) in the DTA apparatus were measured. The results are shown in Fig. 6. At low temperatures (800°C and 900°C), only eucryptite ($LiAlSiO_4$) precipitated, the appearances of glasses were still transparent. Between 900 and 1000°C eucryptite transformed to $LiAlSi_3O_8$ and the sample became opaque. After that, gahnite and willemite precipitated.
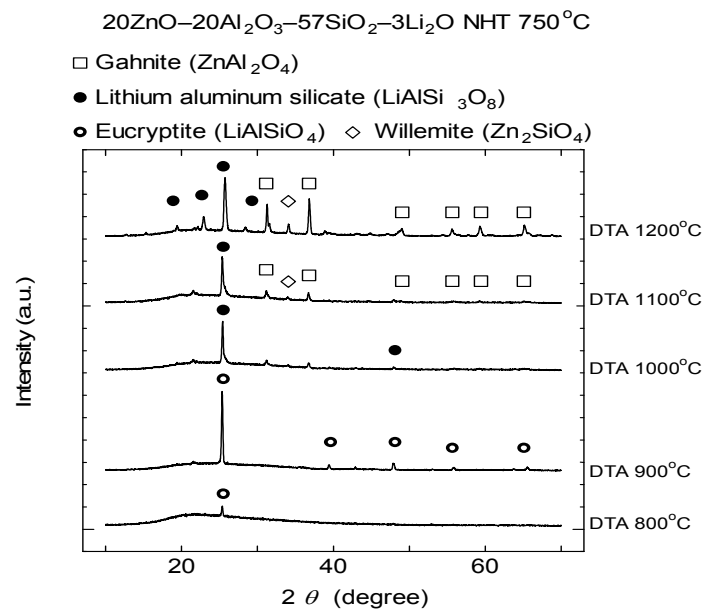

Fig. 6. XRD patterns of 20AZ3Li after stop DTA at various temperatures.

In the sample containing Li_2O, a part of ZnO in the parent glass needs to precipitate as a phase except gahnite because a part of Al_2O_3 is consumed in the precipitation of $LiAlSi_3O_8$. Then, ZnO precipitated as willemite (Zn_2SiO_4) in 20AZ and as $ZnTiO_3$ in 20AZ3Li6T. The addition of TiO_2 suppressed the formation of willemite and accelerated the precipitation of $ZnTiO_3$. On the other hand, the crystallization processes of 20AZ3Li6T are different from 20AZ3Li (Fig. 7). Gahnite precipitated from the lower temperature and it precipitated the same time with spodumene and $LiAlSi_3O_8$ at DTA 900°C. However, all of spodumene changed the form to be $LiAlSi_3O_8$ at DTA 1100°C. Moreover, $ZnTiO_3$ precipitated at DTA 1200°C which means there are rich of ZnO in glassy phase to form with TiO_2 at DTA higher temperature.
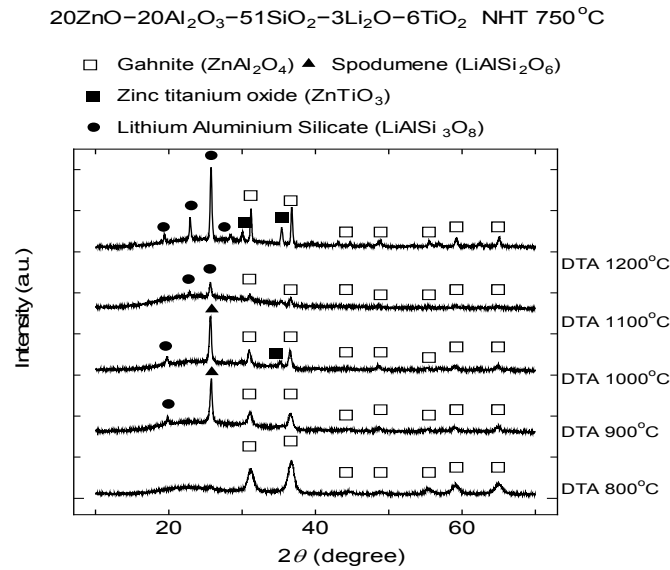
Fig. 7. XRD patterns of 20AZ3Li6T after stop DTA at various temperatures.

In cased of adding Na_2O and K_2O (without TiO_2), only gahnite precipitated as shown in Fig. 8. However, after TiO_2 was introduced in 20AZ3Na6T, gahnite precipitated as a main phase and rutile (TiO_2) precipitated as minor phase.
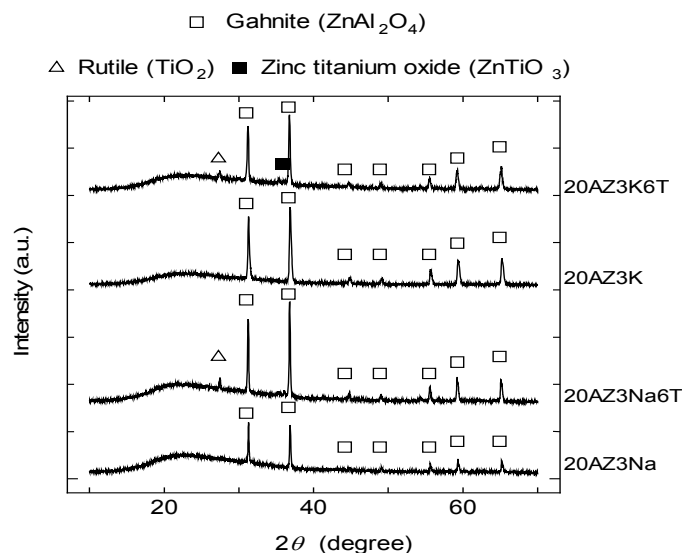

Fig. 8. XRD patterns of as-casted samples after DTA of 20AZ3Na, 20AZ3Na6T, 20AZ3K, and 20AZ3K6T, respectively.

The dependence of crystal sizes of lithium aluminium silicate on NHT temperature for base glass, 20AZ3Li, and 20AZ3Li6T, respectively was shown in Fig. 9. Sizes increased when TiO_2 was added. TiO_2 did not affect to the nucleation rate in this system even though it acts as nucleating agent. According to the appearances of glasses which are shown in Table 3, 20AZ3Li6T showed surface crystallization. That means the crystal growth rate of 20AZ3Li6T if higher than 20AZ3Li. To obtain nanoparticle sizes, high density of volume nucleation should be achieved before crystal begins to grow; therefore crystal growth rate should be slow. That is one possibility of larger sizes of 20AZ3Li6T than 20AZ3Li. As the previous study in this system [22], transparent glasses could be obtained if the sizes were in the range of 10-20 nm. In this case, all samples are opaque and the sizes are in the range of 30-45 nm.
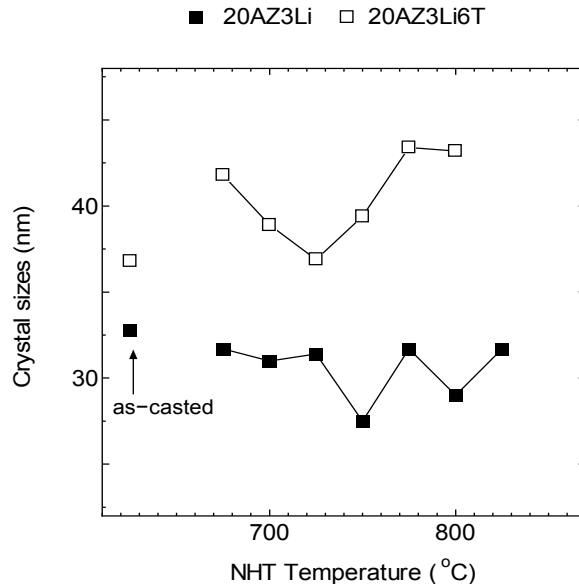
Fig. 9. Relationship between crystal sizes and NHT temperature of 20AZ, 20AZ3Li, and 20AZ3Li6T, respectively.

The effect of alkaline-earth metal oxides addition on the glass transition temperature (T_g), and crystallization peak temperature (T_c) was shown in Fig. 10. When adding only alkaline-earth metal oxides (20AZ3Ca, 20AZ3Sr, 20AZ3Ba), glasses melted during DTA measurement until 1200ºC without showing any clear crystallization peaks. That is due to low viscosity and we could see endothermic peak. DTA was stopped around 1100ºC and the appearances were still transparent. It could be implied that crystal grows during DTA 1100ºC to 1200ºC and sizes are larger than the wavelength of visible light. Light could not pass through the crystal and scattered so the samples became opaque. In case of adding alkaline-earth metal oxides with TiO_2 (20AZ3Ca6T, 20AZ3Sr6T, 20AZ3Ba6T), glasses did not melt or change the form during DTA. Moreover, two crystallization peaks appeared in 20AZ3Sr6T and 20AZ3Ba6T in which gahnite precipitated first and rutile precipitated separately at DTA higher temperature (Fig. 11 and 12).
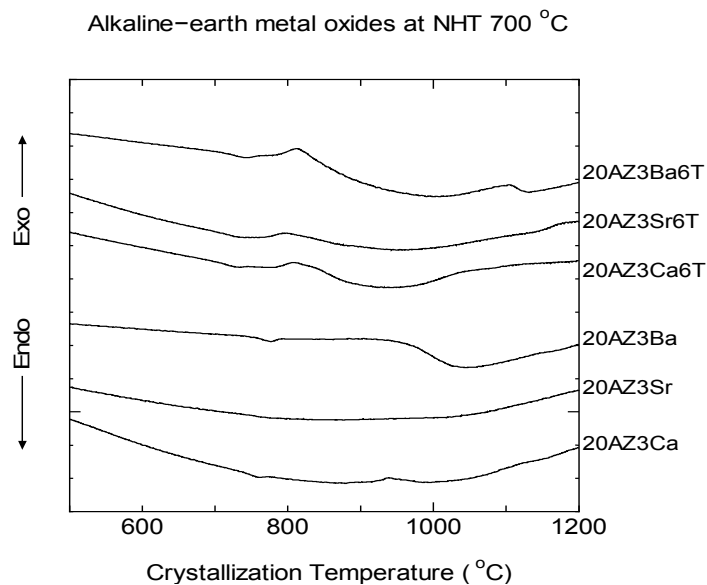

Fig. 10. DTA curves of 20AZ3Ca, 20AZ3Sr, 20AZ3Ba, 20AZ3Ca6T, 20AZ3Sr6T, and 20AZ3Ba6T.
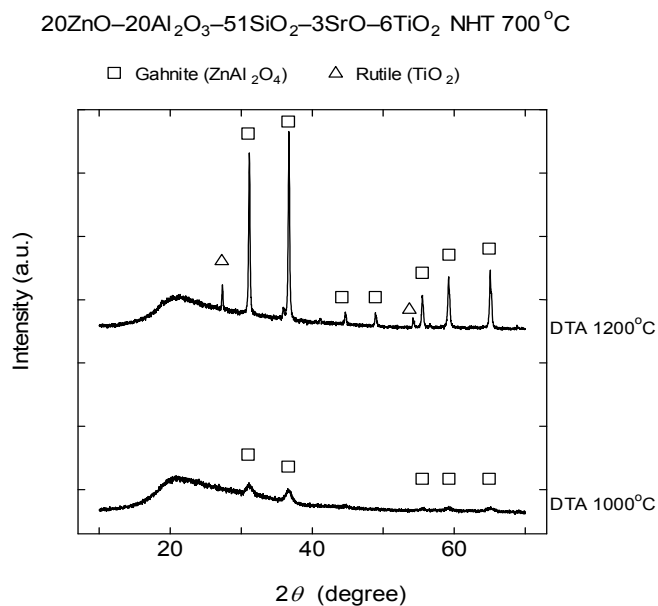
$20ZnO-20Al_2O_3-51SiO_2-3SrO-6TiO_2$ NHT $700\,^{o}C$

Fig. 11. XRD patterns of 20AZ3Sr6T at NHT 700ºC compare between DTA 1000ºC and 1200ºC.

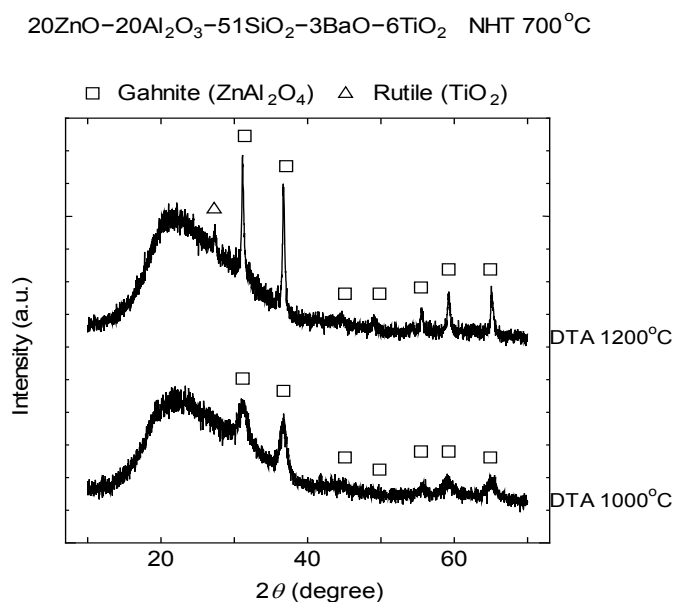$20ZnO-20Al_2O_3-51SiO_2-3BaO-6TiO_2$ NHT $700\,^{o}C$

Fig. 12. XRD patterns of 20AZ3Ba6T at NHT 700ºC compare between DTA 1000ºC and 1200ºC.

The precipitated phases in the sample containing alkaline-earth metal oxides were shown in Fig. 13. Gahnite precipitated as predominant phase in all samples; in addition, rutile precipitated as minor phase when TiO_2 was added. Quartz precipitated as minor phase in 20AZ3Ca, 20AZ3Sr and it was still remain in 20AZ3Ca6T and suppressed in 20AZ3Sr6T.

Alkaline−earth metal oxides at NHT 700 ^{o}C

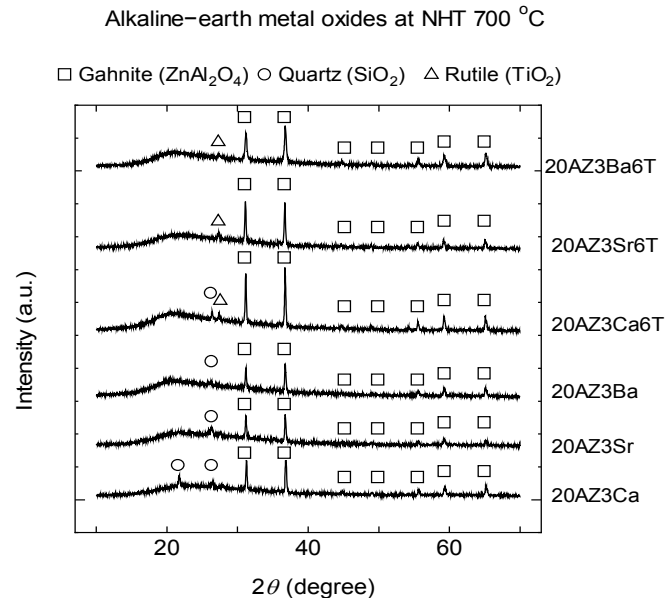□ Gahnite (ZnAl$_2$O$_4$)   ○ Quartz (SiO$_2$)   △ Rutile (TiO$_2$)

Fig. 13. XRD patterns of 20AZ3Ca, 20AZ3Sr, 20AZ3Ba, 20AZ3Ca6T, 20AZ3Sr6T, and 20AZ3Ba6T, respectively.

The dependence of crystal sizes of Gahnite on NHT temperatures for alkaline-earth metal oxides addition was shown in Fig. 14. The sizes of 20AZ3Ca, 20AZ3Ca6T, 20AZ3Sr, 20AZ3Sr6T, and 20AZ3Ba6T were larger than 100 nm. Crystal sizes of 20AZ3Ba6T were around 30-50 nm and smaller than base glass because TiO$_2$ increased number of nuclei. However, the addition of TiO$_2$ did not promote nucleation in the others.
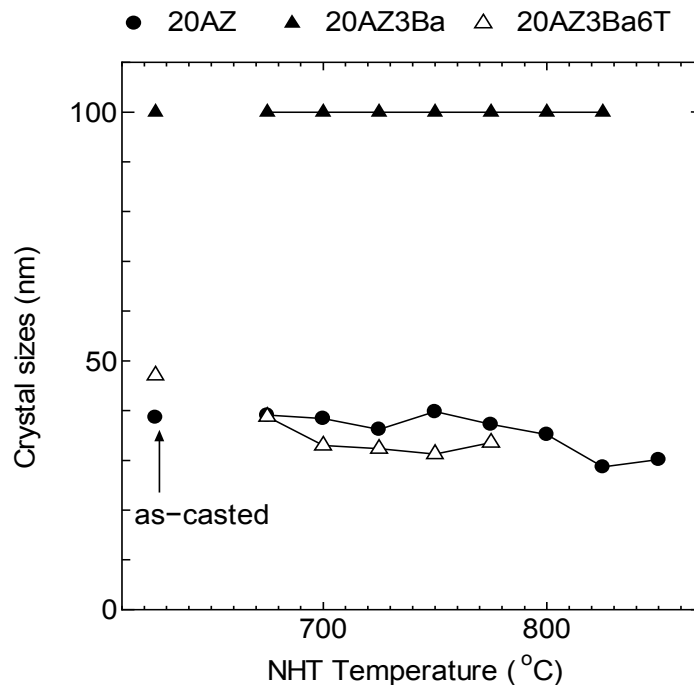

Fig. 14. The relationship between crystal sizes and NHT temperatures of 20AZ, 20AZ3Ba, and 20AZ3Ba6T, respectively.

4. Conclusions

Alkaline metal oxides affected the glass-formation of ZAS glasses. Glasses could be formed when Li_2O was introduced in the system. On the other hand, homogeneous glasses were not obtained when Na_2O and K_2O were added due to the precipitation of gahnite. The precipitation of gahnite was observed in all systems. When 3 mol% of Li_2O was added, lithium aluminium silicate precipitated in the crystallization process as the main phase instead of gahnite and crystallization behaviour changed much. TiO_2 added as a nucleating agent tends to form a compound with ZnO when extra ZnO exists. Because glasses could be formed only when Li_2O addition, crystal sizes are larger than 100 nm when adding Na_2O and K_2O but sizes are around 30-40 nm when adding Li_2O or Li_2O and TiO_2.

All glasses could be formed when adding alkaline-earth metal oxides but they were melted during DTA due to low viscosity. After added TiO_2, all glasses did not melt or change the form and T_c obtained. According to crystalline phases, Gahnite precipitated predominantly and later quartz precipitated; however, quartz was suppressed and rutile precipitated instead after the addition of TiO_2. In case of sizes, only 20AZ3Ba6T are in the range of 30-50 nm, the others are larger than 100 nm.

Acknowledgement

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