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Effect of SnO_2 addition on crystallization of Li_2O-Al_2O_3-SiO_2 glass ceramic

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SnO_2 is adopted as an environmentally friendly fining agent instead of As_2O_3 or Sb_2O_3. Recently, it is reported SnO_2 also works as a nucleating agent. SnO_2 added Li_2O-Al_2O_3-SiO_2 glass was prepared and its crystallization behavior was investigated using XRD and SEM. XRD intensity due to LAS crystalline of Li_2O-Al_2O_3-SiO_2 glass-ceramics became higher as SnO_2 content increased. This result suggests SnO_2 promotes crystallization of Li_2O-Al_2O_3-SiO_2 glass-ceramic. Results were compared to Li_2O-Al_2O_3-SiO_2 glass ceramics containing nucleating agent such as ZrO_2, TiO_2 and P_2O_5. Effect of mixing SnO_2 and ZrO_2 was also investigated.

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Introduction

Li_2O-Al_2O_3-SiO_2 glass ceramic, hereafter called LAS glass ceramic, has excellent characteristics such as transparency, heat resistance and thermal shock resistance, which is used for cooktop, cookware and fireplace window, etc. LAS glass ceramic is obtained through controlled two-step heat treatment consists of nucleation and crystal growth. During heat treatment, β-quartz s. s. firstly crystallizes as a meta-stable phase and partly or completely transforms into β-spodumene s. s. as heat treatment temperature becomes higher.

Glass for LAS glass ceramic mainly consists of LAS crystalline constituent, dissolvable constituent in LAS crystalline, nucleating agent and fining agent.[1] SnO_2 is adopted as an environmentally friendly fining agent instead of As_2O_3 or Sb_2O_3. Recently, it is reported SnO_2 also works as a nucleating agent.[2] However, detail of its effect is not understood well. Purpose of this work is understanding effect of SnO_2 as a nucleating agent in LAS glass ceramic. Results were compared to LAS glass ceramic containing conventional nucleating agent such as ZrO_2, TiO_2 and P_2O_5. Effect of mixing SnO_2 and ZrO_2 was also investigated.

Experimental

Glass with chemical composition of (76-x)SiO_2-14Al_2O_3-1.5RO-8Li_2O-0.5(Na_2O+K_2O)-xMyOz in mol% was prepared using melt quenching method (where RO=MgO+CaO+SrO+BaO and MyOz=SnO_2, ZrO_2, TiO_2 or P_2O_5). The melting temperature was 1650℃ and quenched glass was annealed at 700℃ and was cooled to RT. Prepared samples were heat treated and crystallized. Crystallization behaviors were analyzed by XRD measurements and SEM observations.

Results and Discussion

Figure 1 shows XRD pattern of heat treated SnO_2 free and SnO_2 added sample changing crystal growth temperature(nucleation 790℃-60min crystal growth 900～1100℃-20min). β-quartz s. s. was detected as for SnO_2 free sample. As for SnO_2 added sample, β-spodumene was also detected, especially at high crystal growth temperature. XRD intensity due to LAS crystalline becomes higher by SnO_2 addition. These results suggest SnO_2 works as a nucleating agent and promotes crystallization of LAS glass ceramic.

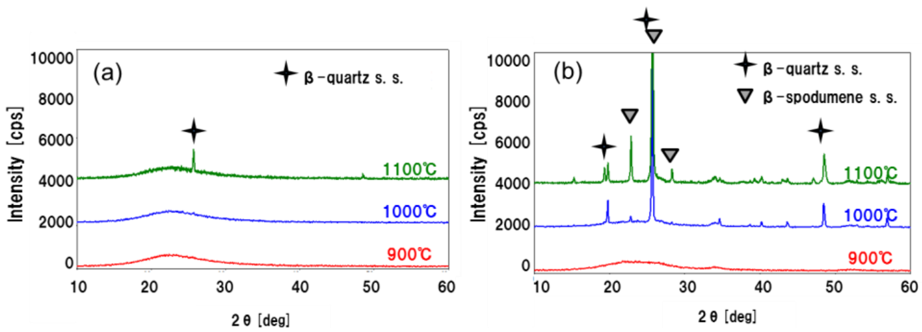

Figure 1. XRD pattern of heat treated (a) SnO2 free and (b) SnO_2 added samples.

To investigate the early stage of crystallization, SnO_2 added sample after heat treatment only for nucleation was prepared. SnO_2 crystalline was detected by XRD before LAS crystalline crystallization. This result indicates SnO_2 crystallize by itself at nucleation stage and promotes LAS crystalline nuclei formation.

Crystallization behavior of SnO_2 added sample was compared to those of ZrO_2, TiO_2 or P_2O_5 added samples. Figure 2 shows XRD intensity of each sample due to LAS crystalline changing crystal growth temperature(nucleation 790℃-60min crystal growth 900～1100℃-20min). SnO_2 or ZrO_2 added samples showed high XRD intensity compared to TiO_2 or P_2O_5 added samples. This result suggests ZrO_2 and SnO_2 strongly promote crystallization compared to TiO_2 and P_2O_5. At early stage of crystallization, ZrO_2 crystalline was detected as for ZrO_2 added sample. However, no crystalline except for β-quartz s. s. was detected as for TiO_2 or P_2O_5 added samples.

SEM observation results indicated SnO_2 and ZrO_2 promote bulk crystallization. As for TiO_2 added sample, droplet like phase was observed, indicating phase separation. LAS crystalline selectively crystallized in droplet like phase.

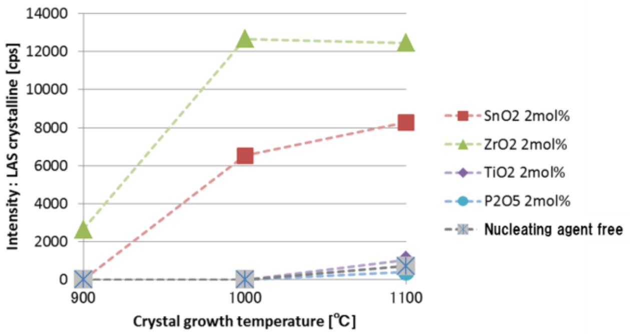

Figure 2. XRD intensity due to LAS crystalline chainging nucleating agent.

According to TEM-EDX analysis, droplet like phase was Ti-Al rich phase. As for P_2O_5 added sample, no crystalline was observed.

Figure 3 shows XRD intensity due to LAS crystalline of SnO_2 and ZrO_2 added samples changing $SnO_2/(SnO_2+ZrO_2)$ (nucleation 790℃-60min crystal growth 900～1100℃-20min). SnO_2 and ZrO_2 added samples showed high XRD intensity compared to that of SnO_2 or ZrO_2 added samples, especially $SnO_2/(SnO_2+ZrO_2)$ is 0.25-0.5. This result indicates mixing SnO_2 and ZrO_2 promotes crystallization.

Figure 4 shows XRD intensity of SnO_2 or ZrO_2 added sample after heat treatment. After 2h heat treatment, SnO_2 was detected but ZrO_2 was not detected. However, after 16h heat treatment, ZrO_2 and LAS crystalline were detected as for ZrO_2 added sample whereas none of LAS crystalline was detected as for SnO_2 added sample.

With above results, crystallization mechanism of SnO_2 and ZrO_2 added sample could be proposed. As glass is heat treated, SnO_2 crystallizes first and acts as a nucleating agent for ZrO_2 crystalline. As a result, crystallization of ZrO_2 is promoted and that of LAS crystalline is promoted as well.

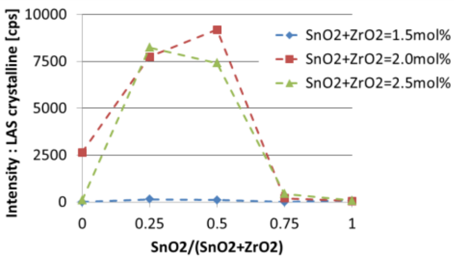

Figure 3. XRD intensity due to LAS crystalline of SnO_2 and ZrO_2 added samples.

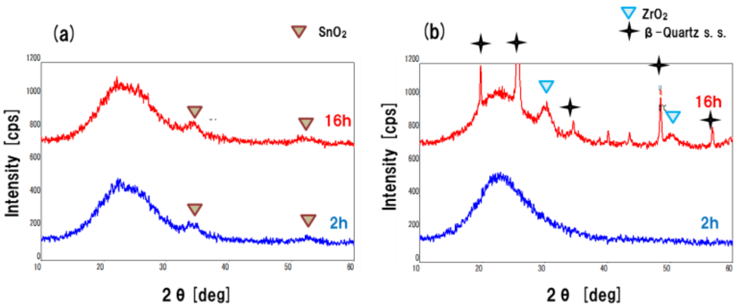

Figure 4. XRD pattern of (a) SnO_2 or (b) ZrO_2 added samples.

Conclusion

Effect of SnO_2 addition on crystallization of LAS glass ceramic was investigated. SnO_2 promoted crystallization of LAS glass ceramic and its effect was high compared to conventional nucleating agent such as TiO_2 and P_2O_5. Mixing SnO_2 and ZrO_2 promoted crystallization of LAS glass ceramic further. SnO_2 might work as a nucleating agent of ZrO_2 crystalline. SnO_2 can be used as a unique constituent which enhances effect of nucleating agent such as ZrO_2.

References

1. Z. Strnad, Glass-Ceramic Materials, 1986, p.96
2. M. Dressler, B. Rudinger, J. Deubener, Journal of Non-Crystalline Solids, Vol. 389, 2014, 60-65