DEPENDENCE OF GLASS-FORMING ABILITY ON STARTING COMPOSITIONS IN Y_2O_3–Al_2O_3–SiO_2 SYSTEM

LIANG WU, #GUANGHUA LIU, JIANGTAO LI, BIN HE, ZENGCHAO YANG, YIXIANG CHEN

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

#E-mail: liugh02@mails.tsinghua.edu.cn

Submitted December 22, 2010; accepted May 28, 2011

Keywords: Glass, Composition, Crystallization, Density

The dependence of glass-forming ability on starting compositions in Y_2O_3–Al_2O_3–SiO_2 (YAS) system has been investigated by melting experiment. Transparent YAS glasses have been prepared under the condition of furnace cooling instead of quenching. It is found that, in the YAS ternary phase diagram, the compositions on the $Y_3Al_5O_{12}$–SiO_2 line and with 52-68 mol% SiO_2 have a higher glass-forming ability to produce pure glass. For the compositions with too much or less SiO_2 or with Y/Al = 5/3, 1/1, or 1/3, crystallization occurs with the formation of $Y_3Al_5O_{12}$, $Y_2Si_2O_7$, $Al_6Si_2O_{13}$, or SiO_2. The densities of the YAS glasses increase with decreasing SiO_2 contents and increasing Y/Al ratios, and for the samples with Y/Al = 3/5 there is a good linear relationship between the density and SiO_2 content.

INTRODUCTION

Y_2O_3–Al_2O_3–SiO_2 (YAS) glasses are widely studied for both structural and functional applications because of their promising mechanical and optical properties [1-3]. YAS glasses can accommodate high concentrations of rare-earth dopants and have great potential for optical applications. For example, based on YAS glasses, $Y_3Al_5O_{12}$-based glass-ceramics can be prepared as yellow phosphors for white LED [4-7].

The properties of YAS glasses strongly depend on their starting compositions. Previous studies have shown that the density, refractive index, thermal expansion coefficient, and hardness of YAS glasses all increase with increasing content of Y_2O_3 [8]. In addition, the starting compositions play an important role in determining the glass-forming ability of YAS system [9]. For most conditions, only some YAS compositions can produce pure glass and the others encounter crystallization.

In this paper, the dependence of glass-forming ability on starting compositions in YAS system is investigated by conventional melting experiment. Totally 12 compositions are studied, as shown in Figure 1, where six ones are located on the SiO_2–$Y_3Al_5O_{12}$ line to study the effect of SiO_2 content, and the other ones are selected with different Y/Al ratios.

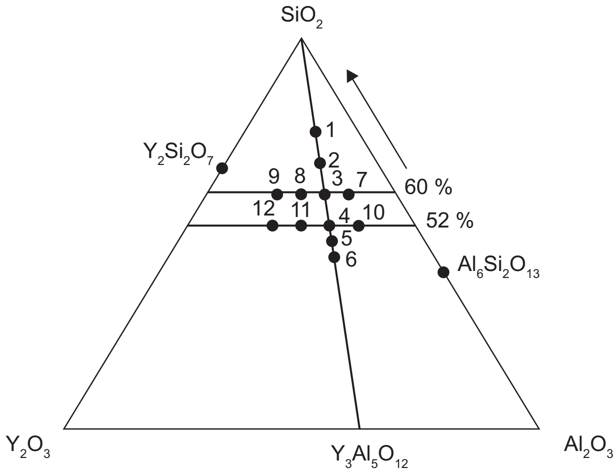


Figure 1. Ternary phase diagram of the Y_2O_3–Al_2O_3–SiO_2 system. The starting compositions investigated in this work are marked by numbers from 1 to 12.

EXPERIMENTAL

Commercial powders of Y_2O_3 (99.999%, Ruike Rare-earth Center, China), Al_2O_3 (99.0%, Jingqiu Chemical Engineering Co., China), and SiO_2 (99.0%, Xilong Chemical Engineering Co., China) were used as raw materials.

The raw materials were mixed according to the proportions listed in Table 1, and homogenized by ball milling for 1 h with ZrO_2 balls as medium and ethanol as solvent. Then, the slurry was fully dried to get the starting reactant powder. Each batch of 10.0 g starting powder was loaded into a corundum crucible and heated in an electric furnace. The temperature was raised from room temperature to 1500°C by a heating rate of 4°C/min. After dwelling for 2 h, the power was switched off and the sample was naturally cooled down in the furnace. The cooling rate varied with temperature and was 4-30°C/min in the range of 800-1500°C. The as-prepared samples were machined and polished for later characterizations.

The bulk density was measured according to the Archimedes principle. The phase assemblage was identified by X-ray diffraction (XRD; D8 Focus, Bruker, Germany) using Cu Kα radiation. The microstructure was examined by scanning electron microscopy (SEM; S-4300, Hitachi, Japan). Energy dispersive spectroscopy (EDS; INCA, Oxford Instrument, UK) was applied for chemical analysis.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the melting experiment for all the investigated compositions. Except for YAS-12, all the other compositions were melted at 1500°C. In the samples of YAS-2, YAS-3, and YAS-4, pure glasses were obtained, and the other samples encountered crystallization. It is evident that the glass-forming ability of a YAS melt strongly depends on its composition.

At first, the content of SiO_2 has a significant effect on the glass-forming ability. In the samples from YAS-1 to YAS-6, the Y/Al molar ratio is fixed to 3/5 and the SiO_2 content gradually decreases from 76 to 44 mol% (Table 1). When the SiO_2 content was in the range of 52-68 mol%, pure glass was obtained. With 48 mol% SiO_2, crystallization took place at the sample surface and the center part remains to be glass. With a further reduction of SiO_2 content to 44 mol%, crystallization

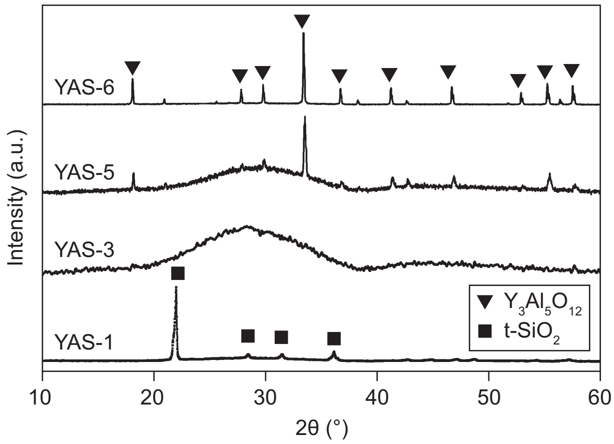


Figure 2. XRD patterns of the samples with different contents of SiO_2 (Y/Al = 3/5).

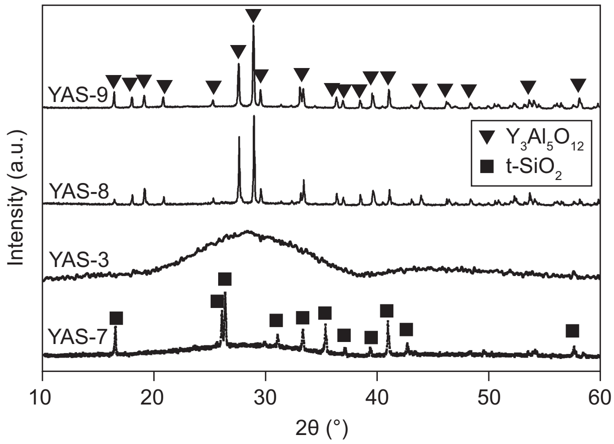


Figure 3. XRD patterns of the samples with different Y/Al ratios (60 mol% SiO_2). In the samples of YAS-7, YAS-3, YAS-8, and YAS-9, the Y/Al molar ratios are 1/3, 3/5, 1/1, and 5/3, respectively.

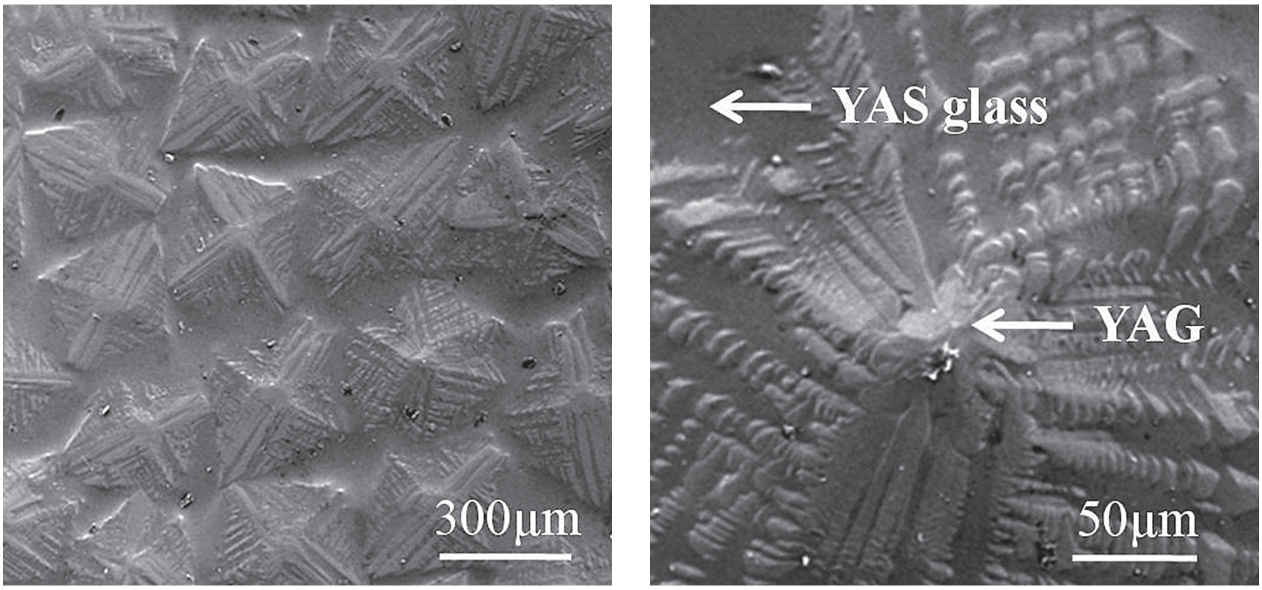
Table 1. Results of the melting experiment for all the investigated compositions.

Sample	Composition (mol%)			Phase assemblage	Density (g/cm^3)	Remarks
	Y_2O_3	Al_2O_3	SiO_2			
YAS-1	9	15	76	SiO_2 + Glass	2.67	Opaque
YAS-2	12	20	68	Glass	3.05	Opaque
YAS-3	15	25	60	Glass	3.25	Transparent, light yellow
YAS-4	18	30	52	Glass	3.44	Transparent, light yellow
YAS-5	19.5	32.5	48	$Y_3Al_5O_{12}$ + Glass	3.54	Crystallization at surface
YAS-6	21	35	44	$Y_3Al_5O_{12}$ + Glass	3.59	Opaque
YAS-7	10	30	60	$Al_6Si_2O_{13}$ + Glass	2.98	Opaque
YAS-8	20	20	60	$Y_2Si_2O_7$ + Glass	3.30	Opaque
YAS-9	25	15	60	$Y_2Si_2O_7$ + Glass	3.33	Opaque
YAS-10	12	36	52	$Al_6Si_2O_{13}$ + $Y_2Si_2O_7$ + Glass	2.99	Opaque
YAS-11	24	24	52	$Y_2Si_2O_7$ + Glass	3.61	Opaque
YAS-12	30	18	52	$Y_2Si_2O_7$ + Glass	3.62	Not melted

occurred in the whole sample and more $Y_3Al_5O_{12}$ was produced, as shown in Figure 2. This is reasonable because SiO_2 is generally accepted as a glass-forming constitute to form the network in glasses. Too much SiO_2, however, is not desirable and induces crystallization of cristobalite, as shown in the sample YAS-1 with 76 mol% SiO_2.

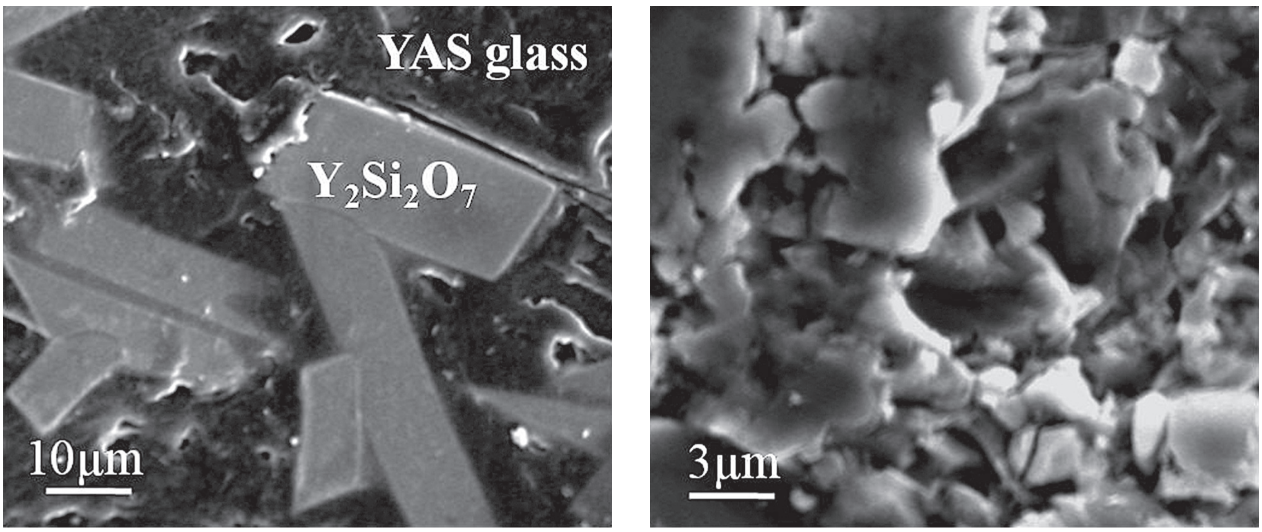
Besides SiO_2 content, Y/Al ratio also affects the glass-forming ability. Figure 3 shows the XRD patterns for the samples with a fixed SiO_2 content of 60 mol% but different Y/Al ratios. It is interesting that only the sample YAS-3 with Y/Al = 3/5 produced pure glass and the other samples encountered crystallization. In the sample YAS-7 rich in Al (Y/Al = 1/3), mullite ($Al_6Si_2O_{13}$) was produced. And in the samples of YAS-8 (Y/Al = 1/1) and YAS-9 (Y/Al = 5/3), $Y_2Si_2O_7$ was obtained. Similar results were observed for the samples with a fixed SiO_2 content of 52 mol%. From the above results, in the YAS ternary phase diagram, the compositions on the $Y_3Al_5O_{12}$-SiO_2 line have a higher glass-forming ability.

Figure 4 shows the SEM images for the surface of the sample YAS-5, where $Y_3Al_5O_{12}$ dendrites are dispersed in YAS glass matrix. The average size of the dendrites is nearly 300 μm, and in each dendrite the gaps among branches are filled with glass. The YAG crystallites and the YAS glass are intersected by each other. From EDS analysis, the glass was rich in Si, and the crystallites had a Y/Al ratio of 0.64, which is close



a) b)

Figure 4. SEM images for the surface of the sample YAS-5. (YAG: $Y_3Al_5O_{12}$).



a) b)

Figure 5. SEM images of the sample YAS-9: (a) at the surface; (b) in the center.

to the stoichiometric ratio of Y/Al=3/5 in $Y_3Al_5O_{12}$. In the sample YAS-5, crystallization was limited at the surface and the rest was still glass, which indicates that crystallization starts from the surface. The exact reason for this surface crystallization is not clear yet. Perhaps it is caused by a higher cooling rate at the surface or a lower energy barrier for nucleation at the interface between the melt and air.

Figure 5 shows the SEM images of the sample YAS-9, in which crystallization occurred with the formation of $Y_2Si_2O_7$. At the surface, coarse plate-like $Y_2Si_2O_7$ crystallites larger than 10 μm are observed with a faceted morphology. In the center, fine $Y_2Si_2O_7$ grains are obtained with an average size below 3 μm. From EDS analysis, the Si/Y ratio in the crystallites is 1.1 and agrees well with the nominal composition of $Y_2Si_2O_7$.

Besides the glass-forming ability, the densities of the samples depend on the starting compositions. For the samples with a fixed ratio of Y/Al=3/5, the density decreases with increasing content of SiO_2, as shown in Figure 6. Especially, in the glass-forming region with a SiO_2 content of 52-68 mol%, a good linear relationship between density and SiO_2 content is observed. For the samples with a fixed SiO_2 content, the density increases with increasing Y/Al ratios.

The real chemical compositions of the as-prepared YAS glasses were determined by EDS analysis. As an example, in the sample YAS-3 the atomic percentages of Y, Al, and Si elements by EDS were 22.1 ± 0.1, 36.7 ± 0.3, and 41.2 ± 0.4, respectively, which agree with its nominal composition (Y = 21.4, Al = 35.7, Si = 42.9). Similar results were obtained for the sample YAS-2 and YAS-4.

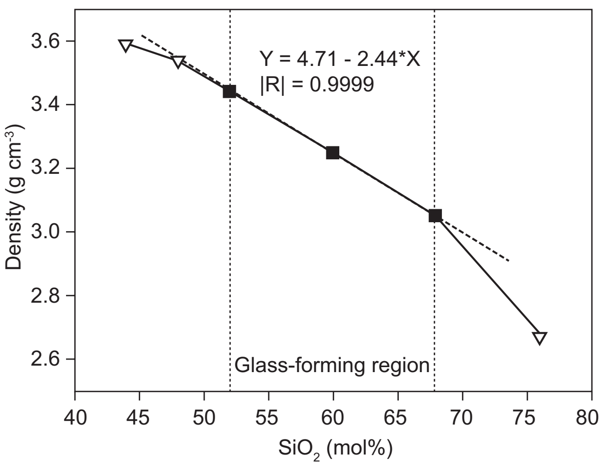


Figure 6. Dependence of the density on the content of SiO_2 for the samples (Y/Al = 3/5).

In addition, the glasses obtained in the samples YAS-3 and YAS-4 showed a light yellow color, which was possibly caused by the presence of impurities (such as Fe) originating from the raw materials.

CONCLUSION

Transparent YAS glasses have been prepared by conventional melting method under furnace cooling instead of quenching. The effect of starting compositions on the glass-forming ability of YAS system has been investigated. It is found that, for a fixed Y/Al ratio of 3/5, pure glass is obtained only when the content of SiO_2 is in the range of 52-68 mol%, and beyond this range crystallization occurs with the formation of $Y_3Al_5O_{12}$ or SiO_2. For a fixed SiO_2 content of 52 or 60 mol%, the compositions with Y/Al = 3/5 have a higher glass-forming ability to produce pure glass, and the other compositions with Y/Al = 5/3, 1/1, or 1/3 encounter crystallization to form $Y_2Si_2O_7$ or $Al_6Si_2O_{13}$. The densities of the YAS glasses increase with decreasing SiO_2 contents and increasing Y/Al ratios. Especially, for the samples with Y/Al = 3/5, a good linear relationship between the density and SiO_2 contents is observed.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Grant No. 50932006, 51002163, and 51001111) and Beijing Natural Science Foundation (Grant No. 2112043).

References

1. Makishima A., Shimohira T.: J. Non-Cryst. Solids *38*, 661 (1980).
2. Erbe E., Day D.E.: J. Am. Ceram. Soc. *73*, 2708 (1990).
3. Tanabe S., Hirao K., Soga N.: J. Am. Ceram. Soc. *75*, 503 (1992).
4. Shunsuke F., Setsuhisa T.: Jpn. J. Appl. Phys. *48*, 12210 (2009).
5. Shunsuke F., Yoshio U., Setsuhisa T.: J. Ceram. Soc. Jpn. *118*, 128 (2010).
6. Mukherjee S., Sudarsan V., Vatsa R.K., Tyagi A.K.: J. Lumin. *129*, 69 (2009).
7. Shunsuke F., Setsuhisa T.: Opt. Mater. *32*, 886 (2010).
8. Hyatt M.J., Day D.E.: J. Am. Ceram. Soc. *70*, 283 (1987).
9. Harrysson R., Vomacka P.: J. Eur. Ceram. Soc. *14*, 377 (1994).