

The XIII International Conference on the Physics of Non-Crystalline

Solids

Crystallization of Yttrium and Samarium Aluminosilicate Glasses

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Abstract

Aluminosilicate glasses containing samarium and yttrium (SmAS and YAS glasses) exhibit high glass transition temperatures, corrosion resistance, and glass stability on heating which make them useful for technological applications. Yttrium aluminosilicate glass microspheres are currently being used for internal selective radiotherapy of liver cancer. During the preparation process, crystallization needs to be totally or partially avoided depending on the final application. Thus knowing the crystallization kinetics can help to prevent or avoid it, by designing a proper thermal pathway. In this work we studied the crystallization kinetics of YAS and SmAS glasses. It was found that both, YAS and SmAS glasses crystallize from the surface. SmAS glass presented lower densities of nucleation sites. The results also showed that the crystal growth apparent enthalpy is larger for SmAS glasses.

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Selection and peer-review under responsibility of Prof. Xiujian Zhao, Wuhan University of Technology

Keywords: yttrium aluminosilicate glass, samarium, aluminosilicate glass surface crystallization, glass-ceramic.

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1. Introduction

Samarium and yttrium aluminosilicate glasses (SmAS and YAS glasses) exhibit high glass transition temperatures, corrosion resistance, and glass stability on heating which make them interesting materials for different applications [Sadiki et al, 2006]. Yttrium aluminosilicate glasses are currently being used for internal selective radiotherapy of liver cancer [Ehrhardt et al, 1987] and are proposed as host matrix for nuclear wastes immobilization [Sadiki et al, 2006 , Prado et al., 2012]. ^{89}Y which is present in nature as a stable isotope can be used for preparing the glasses from which microspheres are made. Neutron activation of the microspheres, produces mainly ^{90}Y through the nuclear reaction $^{89}\text{Y} + n \rightarrow ^{90}\text{Y}$, being the reaction product a beta emitter useful for liver internal radiotherapy. SmAS and YAS glasses are also of interest for internal radiotherapy. During the glass preparation process, crystallization needs to be totally or partially avoided depending on the final application. For radiotherapy or waste immobilization applications [Zanotto et al, 2001 , Prado et al., 2002, Prado et al., 2008] we are interested in fully avoiding crystallization, thus the knowledge of the nucleation and crystal growth kinetics is mandatory. In this work we studied the crystallization kinetics: surface density of nucleation sites [Lago et al, 2012 , Muller et al., 2000], and crystal growth rate at different temperatures.

2. Experimental Methods

2.1. Glass preparation and glass transition temperature determination

YAS glass samples were prepared with composition: 35 % SiO_2 , 20 % Al_2O_3 and 45 % Y_2O_3 (wt %) which corresponds approximately to the core of the ternary glassy domain [White et al, 1994]. A mixture of the precursor oxide powders was homogenized in a rotating mill and melted in a platinum crucible for two hours at 1600 °C. The melt was poured on a stainless steel plate and immediately splat-cooled with a second steel plate.

SmAS glass samples 35 % SiO_2 , 20 % Al_2O_3 and 45 % Sm_2O_3 (wt %) was prepared following the procedure previously described for YAS glass.

Sigma Aldrich Y_2O_3 purity 99,99%, Sm_2O_3 99,9% purity, Al_2O_3 99,7% purity, Quartz-Fluka Analytical SiO_2 , purity 99,865% purity were used.

Differential thermal analysis experiments were performed on powdered samples of each glass. The analysis was carried out over a temperature range 20 °C to 1300 °C at a heating rate of 10 °C · min⁻¹. The glass transition temperature T_G , crystallization beginning temperature T_C , and temperature T_X corresponding to the crystallization peak were determined from the measurements.

2.2 Crystallization

2.2.1 X-Ray Diffraction Experiments

XRD measurements were performed with a diffractometer Bruker D8 Advance at a wavelength 0.154054 nm. Scans were performed in the range 10°- 90° with a step size of 0,01°. The samples were glass powder with a particle size below 50 microns for SmAS glass, and surface crystallized plates for YAS glasses, after 72 and 24 hours of heat treatment at 1000 °C, respectively. Crystal phase identification was made through comparison of the diffraction patterns with that of XRD cards for known crystalline phases.

2.2.2 Surface density of nucleation sites

To determine the surface density of nucleation sites, N_s , heat treatments were performed on YAS glass

samples (obtained by splat cooling) during 1, 2, 4, 6, 10 and 15 hours at $1000, 1020$ and 1040 ± 2 °C; and SmAS glass samples (obtained by splat cooling) during 6, 15, 24, 30, 40 and 50 hours at 980 and 1000 ± 2 °C.

After each heat treatment, the number of crystals per unit area was determined, using optical microscopy in those cases where crystals were not impinging among them. Surface density of nucleation sites was determined assigning a nucleus to each surface crystal.

Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) was used to partially characterize the crystalline phases present in the samples at the various stages of growth.

2.2.3 Crystal Growth rate

Cross sections of the samples were cut, polished up to 3 micron diamond paste and etched with a 2 % HF, water solution for 60 seconds. Crystal growth rates were measured by the slope of the measured quantities crystal size vs time. At short heating times, when crystals do not impinge on each other, the crystal size was measured as half its larger dimension. But when a complete crystalline layer was formed, crystal size was measured as the layer thickness.

3. Results and discussion

3.1. Thermal analysis

Glass transition temperature (T_g) and DTA peak crystallization temperatures (T_x) were determined by differential thermal analysis (DTA) with a SDT-Q600 TA instrument. Measurements were done on small pieces of glass, placed in an alumina crucible. The reference crucible is an empty alumina crucible. Experiments were carried out up to 1350 °C with a heating rate of 10 °C·min⁻¹.

The results of the DTA analysis are resumed in Table 1. From the results we determined that the crystallization peak starts at temperature of $T_c = 1143$ and 1057 °C for YAS and AS-Sm slab, respectively.

Table 1. Glass transition and crystallization temperatures for both glasses.

Glass	Glass Transition Temperature T_g (°C)	DTA crystallization peak Temperature (°C)	DTA crystallization beginning Temperature (°C)
YAS	921	1243	1143
AS-Sm	890	1171	1057

AS-Sm has the same value for T_x - T_g , but both temperatures (T_x and T_g) are lower than for YAS glass.

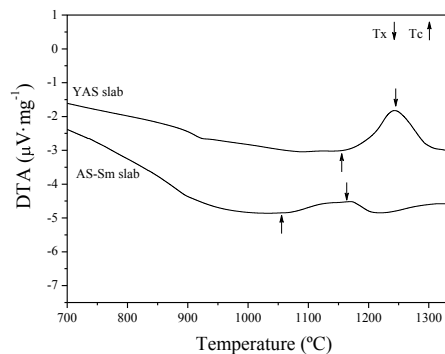


Fig. 1. T_c and T_x determined by DTA for different glasses.

3.2. Identification of the crystalline phases

From the diffractograms obtained by X-ray diffraction of crystallized YAS glass, it was found yttrium disilicate ($Y_2Si_2O_7$, pattern number 38-0223, crystalline system: anorthic), mullite ($Al_2.3Si_{0.7}O_{4.85}$, pattern number 1-074-2419; crystalline system: orthorhombic) and sillimanite (Al_2SiO_5 , pattern number 1-074-0274; crystalline system: orthorhombic). They agree with published data by Arita et al., 1992, and Hyatt et al. 1987 but unlike the work of O'Meara et al., 1987, because we did not detect alumina.

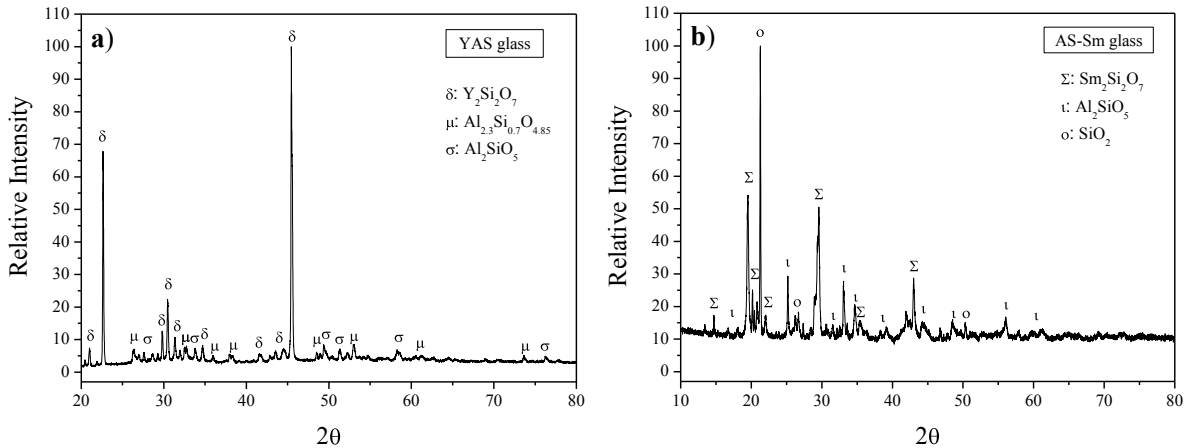


Fig. 2 a). X-ray diffraction pattern of crystallized YAS glass after 24 hours heat treatment at 1000 °C, where δ : yttrium disilicate, σ : sillimanite, μ : mullite. b) X-ray diffraction pattern of crystallized AS-Sm glass after 72 hours heat treatment at 1000 °C, where Σ : samarium disilicate, o: silicon dioxide, t: sillimanite.

The phases detected are in general agreement with those expected from the equilibrium ternary phase diagram, namely $Y_2Si_2O_7$, SiO_2 and mullite.

In the case of crystallized SmAS, we identified the presence of samarium disilicate ($Sm_2Si_2O_7$, pattern number 48-0053, crystalline system: Monoclinic), silica (Si_2O , pattern number 48-0476, crystalline system: unknown), and sillimanite (Al_2SiO_5 , pattern number 1-0741976, crystalline system: Anorthic). The first two phases are consistent with results reported in the literature [Erbe et al., 1990].

3.3. Chemical analysis

To complement the information obtained by XRD, both glasses after the crystallization process described in 2.2, were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Through this analysis, $Y_2Si_2O_7$ crystals were identified in crystallized YAS glass. As shown in Fig. 3 and Table 2, surface crystals are highly enriched in yttrium, and the relationship Y/Si is very close to that of yttrium disilicate.

Table 2. (*) Chemical analysis of YAS crystals shown in Figure 4a. (1000 °C – 1h) (**) Yttrium disilicate values as reference.

Chemical Analysis (wt %)		
Al	Si	Y
(*) 9,92	23,51	66,57
(**)0	24	76

The YAS glass molar composition is $3\text{SiO}_2 \cdot 1\text{Y}_2\text{O}_3 \cdot 1\text{Al}_2\text{O}_3$. Formation of yttrium disilicate $2\text{SiO}_2 \cdot 1\text{Y}_2\text{O}_3$, lets 1SiO_2 and $1\text{Al}_2\text{O}_3$ remaining. Sillimanite $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ could consume all this remaining glass, agreeing with literature data [Prado et al., 2012], instead Mullite $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ formation would leave Al_2O_3 free. We detected both, Sillimanite and Mullite, but not alumina, the latter could be in small quantities.

In the case of crystallized AS-Sm glass, at least four different morphologies were observed on the crystallized surface.

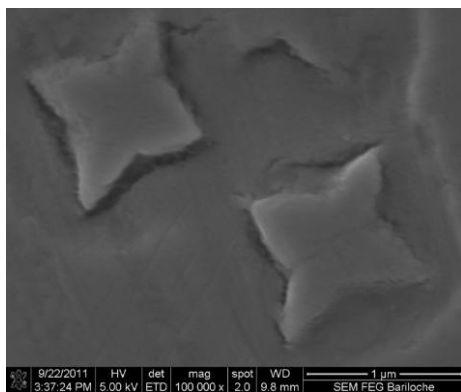


Fig. 3 Surface Yttrium disilicate crystals.

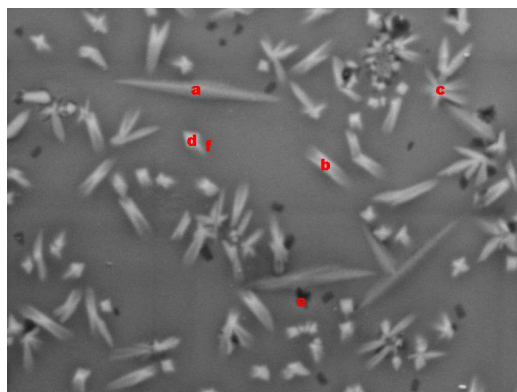


Fig. 4 Crystallized SmAS glass surface.

Table 3. Chemical analysis of SmAS crystals shown in Figure 4. *Matrix near crystal d.

	Chemical Analysis (wt %)					
	Crystal a	Crystal b	Crystal c	Crystal d	Crystal e	Matrix f*
Al	20,15	18,16	16,41	15,02	16,07	20,43
Si	27,97	26,00	23,98	24,09	29,68	27,17
Sm	51,88	55,84	59,61	60,89	54,26	52,40

The main phase appearing on heating on the glass surface of SmAS glass is samarium disilicate at $980\text{ }^\circ\text{C}$ and $1000\text{ }^\circ\text{C}$.

3.4. Surface density of nucleation sites

The main phase appearing on heating on the glass surface of YAS glass is yttrium disilicate [Lago et al., 2012] at $1000\text{ }^\circ\text{C}$ and $1020\text{ }^\circ\text{C}$. The value of the surface density of nucleation sites (N_s) measured for this glass at $1000\text{ }^\circ\text{C}$ was about 10^{11} m^{-2} .

The value of the surface density of nucleation sites (N_s) measured for this glass at $980\text{ }^\circ\text{C}$ was about 10^{10} m^{-2} . The SmAS glass showed the lowest N_s values. See Fig. 5 for the N_s values measured.

3.5. Surface Crystal Growth Rate

Crystal size or the thickness of the crystalline layer observed on the glass cross section resulting from the crystallization heat treatment was measured. Subsequently, the crystal growth rate was determined and the values obtained for YAS glass were: $(8,21 \pm 0,06)\text{ }\mu\text{m} \cdot \text{h}^{-1}$, $(8,05 \pm 0,07)\text{ }\mu\text{m} \cdot \text{h}^{-1}$ and $(13,1 \pm 0,04)\text{ }\mu\text{m} \cdot \text{h}^{-1}$ at 1000 , 1020 and $1040 \pm 2\text{ }^\circ\text{C}$, respectively. In the case of AS- Sm the values obtained were: $(0,12 \pm 0,011)\text{ }\mu\text{m} \cdot \text{h}^{-1}$ and $(0,35 \pm 0,036)\text{ }\mu\text{m} \cdot \text{h}^{-1}$ at 980 and $1000 \pm 2\text{ }^\circ\text{C}$.

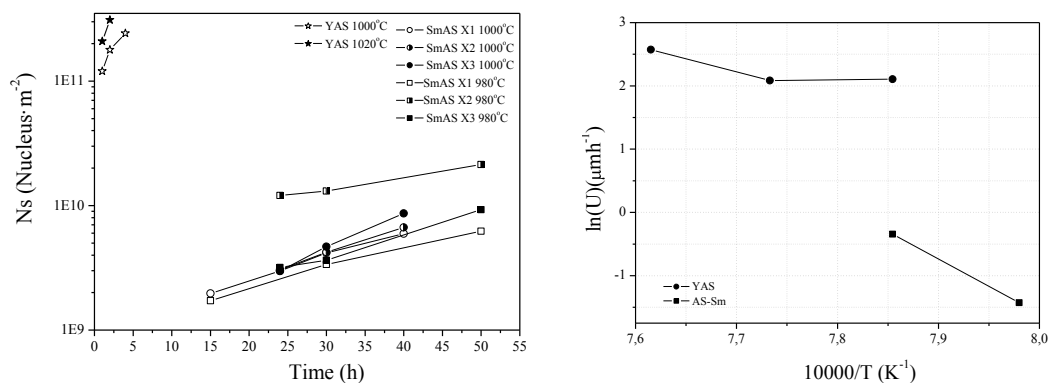


Fig. 5 (left). Density of surface nucleation sites for both glasses at different temperatures, after different times of heat treatment. Fig. 6 (Right). Crystal growth rate as a function of temperature for both glasses.

4. Conclusions

Two homogeneous aluminosilicate glasses were prepared, containing Y or Sm.

After heat treatment 24 hours at 1000 °C, the main surface crystalline phases observed by XRD were the disilicates of the main glass structure modifier (Y or Sm) and sillimanite. Moreover YAS glass surface presented mullite crystals and SmAS glass silicon dioxide crystals.

Optical microscopy observation of the crystallized surface showed yttrium disilicate crystals on YAS. However crystals appearing on SmAS glass surface could not be associated with XRD results .

SmAS exhibited lower surface density of nucleation sites and crystal growth rates than YAS. These facts suggest than SmAS is a good candidate for producing microspheres for microbraquitherapy through the propane-oxygen method.

Acknowledgements

We acknowledge Mr Cacho Cotaro for the micrograph taken with SEM_FEG at Materials Characterization Department and all Nuclear Materials members. Also we would like to acknowledge ANPCyt for funding through project PICT – CNPq 2008-39.

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