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Yttrium SiAlON Glasses: Ultrasonic Study of Crystallisation

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Abstract

The possibilities offered by the use of ultrasonic techniques for the study of the crystallisation of glasses are illustrated in the case of some grades of glasses belonging to the Y–Si–Al–O–N system. © *1997 Elsevier Science Limited.*

Résumé

Les possibilités offertes par l'utilisation des techniques ultrasonores pour l'étude de la cristallisation des verres sont illustrées dans le cas de différentes nuances de verres élaborées dans le systéme Y–Si–Al–O–N.

1 Introduction

Structural transformations affect materials stiffness which is characterised by the elastic moduli. The elastic moduli can be deduced from the measurements of the velocity of ultrasonic pulses propagating through the material.[1,2]

2 Experimental Techniques and Material

Young's modulus was measured using an ultrasonic device especially designed for high temperature applications.[3] The data analysis is based on the 'long bar approximation' in which Young's modulus is related to the compressional ultrasonic wave velocity, V_c, by

$$E = \rho V_c^2$$

where ρ is the density.

The compositions of the glasses are illustrated in Fig. 1, showing the 17 equivalent %N plane section of the Janecke prism at 1700°C. The formula of the glasses in atomic percent is given in Table 1 together with the experimental amount of nitrogen. The crystallisation of these glasses is complex and depends on their chemical composition and on the temperature of the heat-treatments. The $Y_{40}Si_{56}Al_4O_{83}N_{17}$ grade is the closest grade to yttrium disilicate in the glass forming region and yttrialite (y-$Y_2Si_2O_7$) is the phase that forms first. In the $Y_{28}Si_{56}Al_{16}O_{83}N_{17}$ grade, yttrialite is also the first phase that crystallises, whereas it is B-phase (Y_2SiAlO_5N) that precipitates first in $Y_{35}Si_{45}Al_{20}O_{83}N_{17}$.

3 Results

Figure 2 shows a typical curve of the change in Young's modulus during an experiment at constant heating and cooling rates for an oxynitride glass. Young's modulus decreases slowly and linearly up to the glass transition temperature, T_g. Above T_g, it decreases quickly with the glass viscosity, up to a temperature, T_c, where it starts increasing. After cooling at room temperature, Young's modulus is higher than that of the initial glass. The increase in Young's modulus is associated with the formation of crystalline phases, which always have a higher stiffness than the parent amorphous material. T_c is the temperature where the increase in stiffness due to the growing crystallites compensates the decrease resulting from the softening of the glass. The value of T_g and T_c are given in Table 2.

3.1 Grade $Y_{40}Si_{56}Al_4O_{83}N_{17}$

During a first run (Fig. 3), a sample was heated at 5°C min^{-1} up to T_c (1080°C) and held at this temperature until Young's modulus levelled off ($dE\,dt^{-1} < 1$ GPa h^{-1}). Young's modulus increased very quickly during the first hour. Then, the rate of change became very slow and the modulus remained nearly constant after 28 h of heat

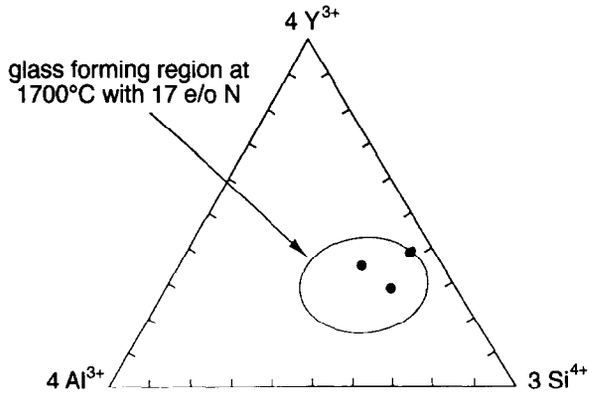

Fig. 1. Plane section at 17 eq% N of the Janecke prism of the YSiAlON system.

Table 1. Composition of the glasses

Grade eq%	*Composition at% (theoretical)*					*At%*
	Y	*Si*	*Al*	*O*	*N*	*N(Exp)*
$Y_{40}Si_{56}Al_4O_{83}N_{17}$	17·58	18·46	1·76	54·73	7·47	7·3
$Y_{28}Si_{56}Al_{16}O_{83}N_{17}$	12·31	18·46	8·35	54·73	7·47	6·8
$Y_{35}Si_{45}Al_{20}O_{83}N_{17}$	15·20	14·66	8·69	54·07	7·38	7·1

treatment. After cooling, the sample was reheated up to 1100°C. Figure 4 shows that the change in Young's modulus was then linear and reversible in the entire temperature range investigated. X-ray diffraction revealed the crystallisation of y-$Y_2Si_2O_7$, that is consistent with the composition and structure of the glass, close to that of yttrium disilicate.[4]

3.2 Grade $Y_{28}Si_{56}Al_{16}O_{83}N_{17}$

The same procedure was used to study the crystallisation of this grade. The soaking temperature was 1085°C. Crystallisation appeared to proceed in three stages (Fig. 5). After a rapid increase during the first hour, Young's modulus levelled off before starting to increase further after 5 h. The rate of change was slow and sigmoidal during this second stage which was followed by a third stage with very similar kinetics. After 25 h, Young's modulus remained constant.

Table 2. Glass transition temperature, T_g, and temperature of the onset of crystallisation, T_c

Grade at%	*Tg US °C*	*Tg Creep °C*	*Tc °C*
$Y_{40}Si_{56}Al_4O_{83}N_{17}$	935	960–980	1080
$Y_{28}Si_{56}Al_{16}O_{83}N_{17}$	925	930–945	1085
$Y_{35}Si_{45}Al_{20}O_{83}N_{17}$	921	935–950	1060

The crystallisation of this grade was also investigated using X-ray diffraction. Figure 6 shows the phases formed as a function of time during an isothermal treatment at 1100°C. The first phase to crystallise is y-$Y_2Si_2O_7$ which partially converts into δ after 24 h. In addition, Y_2SiO_5 and yttrium aluminium garnet (YAG) are also observed after 24 h of treatment.

3.3 Grade $Y_{35}Si_{45}Al_{20}O_{83}N_{17}$

Although the crystallisation of this grade is complex and leads to the formation of two completely different phase assemblages below and above 1200°C, heat treatments at temperatures lower than 1100°C produce B-phase + glass only. An in-depth study of the crystallisation kinetics of this grade has been conducted[5] and is to be published elsewhere.

3.4 Isothermal treatments

Isothermal treatments in the temperature range between T_g and T_c were carried out to determine the incubation period for crystallisation. During an isothermal run, the smallest change in Young's modulus that is detectable is $\Delta E/E \approx 2 \cdot 10^{-3}$.

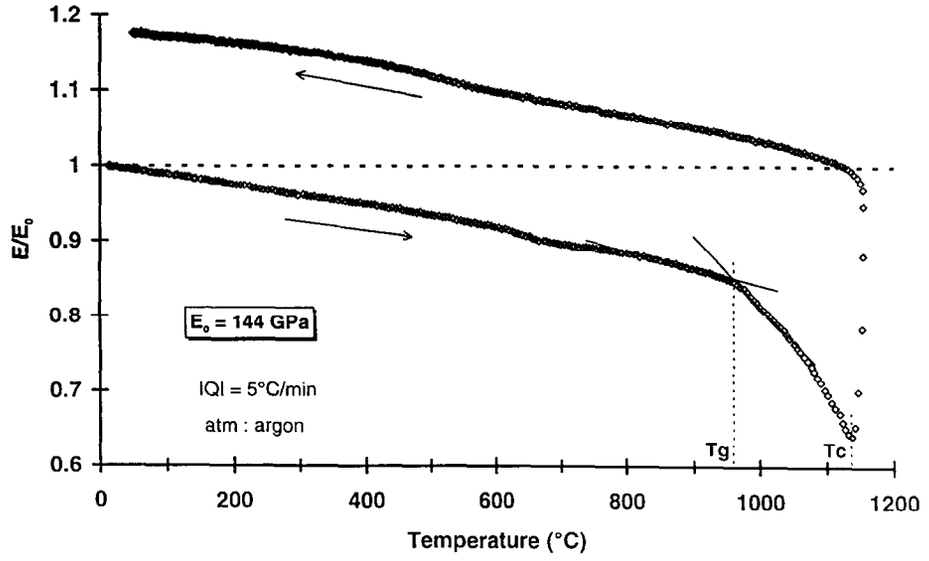

Fig. 2. Changes in Young's modulus with temperature for $Y_{40}Si_{56}Al_4O_{83}N_{17}$ grade.

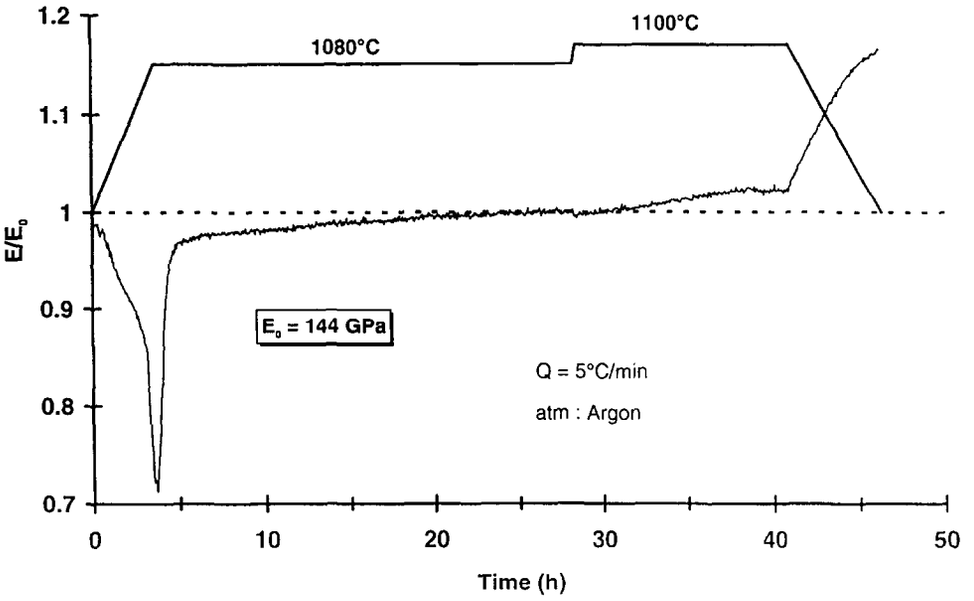

Fig. 3. Change in Young's modulus with time at the crystallisation temperature for $Y_{40}Si_{56}Al_4O_{83}N_{17}$ grade.

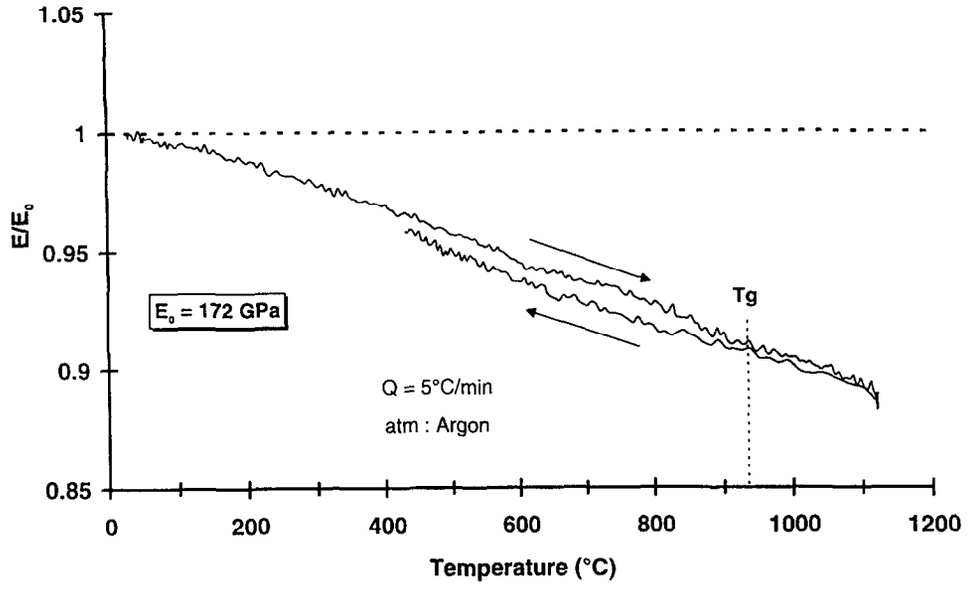

Fig. 4. Change in Young's modulus during heating and cooling for a sample previously heat-treated for 28 h at 1080°C.

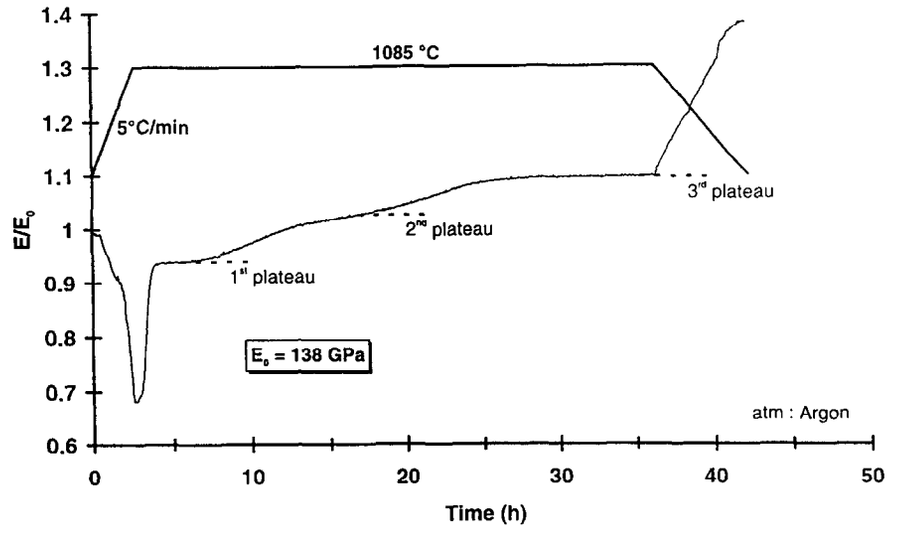

Fig. 5. Change in Young's modulus with time at the crystallisation temperature for $Y_{28}Si_{56}Al_{16}O_{83}N_{17}$ grade.

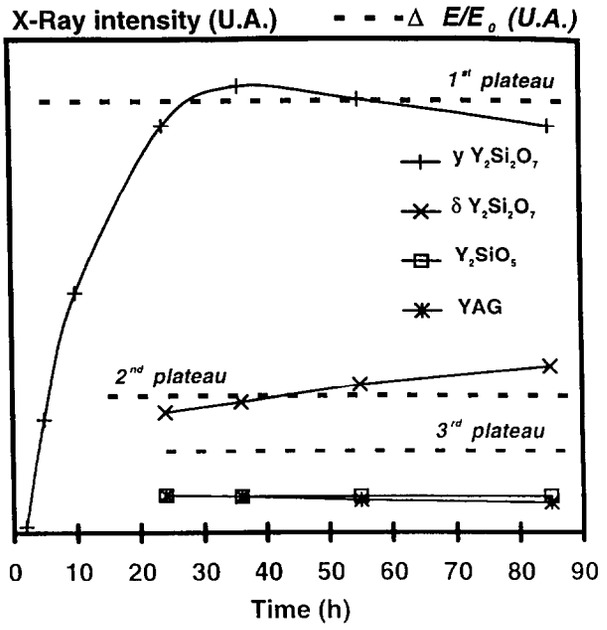

Fig. 6. X-ray intensities of the phases observed after heat treatment at 1100°C for various times. The modulus increases for the three stages observed during the crystallisation are added for comparison.

The complete crystallisation corresponding roughly to $\Delta E/E \approx 0{\cdot}4$, the smallest volume fraction of crystalline phase that can be detected is estimated to be 0·5% and is taken as representative of the start of the crystallisation. The corresponding curves are shown in Fig. 7 on a Time–Temperature–Transformation diagram.

4 Discussion

In the case of the $Y_{40}Si_{56}Al_4O_{83}N_{17}$ grade, the fact that no change was observed in the glass temperature domain during the second run indicates that crystallisation is almost complete, or that the residual glass has a T_g higher than 1000°C.

For $Y_{28}Si_{56}Al_{16}O_{83}N_{17}$, the increase in Young's modulus associated with the first, second, and third plateaus are in the same ratios as the peak intensities corresponding to y-$Y_2Si_2O_7$, δ-$Y_2Si_2O_7$ and Y_2SiO_5 + YAG. Hence, this might suggest that the initial rise is associated with the crystallisation of yttrialite and that the two further increases are due to the formation of δ-$Y_2Si_2O_7$ on the one hand and to that of Y_2SiO_5 and $Y_3Al_5O_{12}$ on the other. In the XRD experiments, the y-$Y_2Si_2O_7$ phase appears to be fully developed after 25 h of treatment whereas the US technique shows that the precipitation is complete after 5 h. Contrary to XRD, that can only detect crystals greater than a critical size, the ultrasonic (US) technique is sensitive to any change in stiffness, whatever the size of the particles. The difference observed between the two techniques, which might be linked to a coarsening stage, emphasises the high sensitivity of the US technique.

Experiments in the temperature domain around T_c and above allow study of the crystallisation. In particular, in the case of a single crystalline phase formation, it is possible to link the mean elastic moduli change to the phase volume fractions by means of Voigt's and Reuss' bounds.[6] Furthermore, isothermal treatments allow study of the crystallisation kinetics.

5 Conclusion

This brief paper illustrates some aspects in which US techniques can contribute to the investigation of glass crystallisation: determination of T_g and

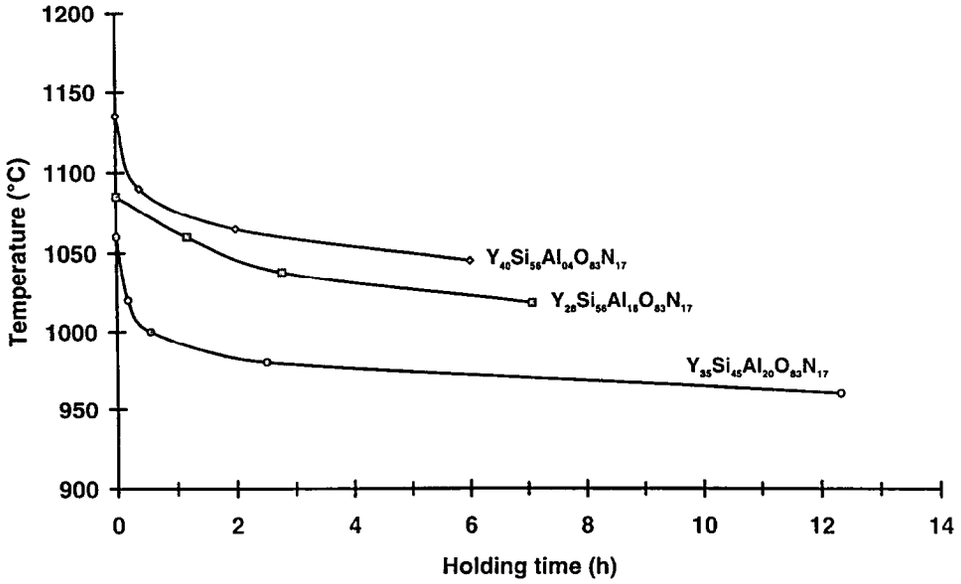

Fig. 7. Time–Temperature–Transformation diagram.

T_c; drawing of Time–Temperature–Transformation diagrams; *in-situ* study of crystallisation kinetics.

Acknowledgements

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