

KINETIC STUDY OF YTTRIUM ALUMINOSILICATE GLASSES CRYSTALLIZATION BY ISOCONVERSIONAL METHODS

D.C. LAGO¹ and M. O. PRADO^{1,2,3}

¹ Nuclear Materials Department. Bariloche Atomic Centre – National Atomic Energy Commission. San Carlos de Bariloche, Argentina.

² National Council of Scientific and Technical Research, Argentina.

³ Balseiro Institute (Cuyo National University, National Atomic Energy Commission). San Carlos de Bariloche, Argentina

Abstract

Vitrification is a particularly attractive immobilization route for HLW due to the chemical durability of the glassy product. Nevertheless, one of the main quandaries is the crystallization of the melt during the cooling, which may affect the durability of the final waste form. Although glass crystallization is considered a common problem, chemically durable glass ceramics can be produced with controlled crystallization. The non-isothermal crystallization kinetics of two yttrium aluminosilicate glasses, were studied. A set of DTA measured at different heating rates, was analyzed using Kissinger, Ozawa and Augis-Bennett isoconversional methods. These methods allow the dependence of the activation energy on the extent of the conversion to be determined. The results obtained show that the activation energy of crystallization process is not constant and varies with temperature. This variation indicates that the transformation kinetics from amorphous to crystalline phase is a complex process involving physical parameters as solid-liquid surface tension, viscosity of the liquid phase and species diffusion in a chemically changing glassy matrix when crystallization is not stoichiometric as in this case. The activation energy dependence observed by the isoconversional method seems to be an interesting tool for the analysis of complex solid state reactions.

Theoretical Basis

The transformation rate for a solid state reaction is generally assumed as the product of two functions, one dependent on the temperature (T) and the other dependent on the conversion fraction (α), can be described by:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$

$f(\alpha)$ is the reaction model, α represents the volume of the crystallized fraction. The reaction rate constant $k(T)$ has an Arrhenian temperature dependence:

$$k(T) = A \cdot \exp\left(\frac{-E}{RT}\right) \quad \text{Combining both Eq:} \quad \frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha)$$

Under non-isothermal conditions with a constant heating rate $\beta = dT/dt$

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \left(\frac{1}{\beta}\right) = \frac{A}{\beta} \cdot \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha)$$

The integral form of the reaction model can be obtained as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E}{RT}\right) dT = \frac{A}{\beta} \cdot I(E, T)$$

Using the isoconversional method, n experiments are carried out at different β and E be determined at any particular value of α , where the integral is:

$$I(E, T) = \int_0^t \exp\left(\frac{-E}{RT}\right) dt \quad \text{There are different mathematical expressions for fitting the experimental data:}$$

The Kissinger method: The Ozawa method: The Augis-Bennett method:

$$\ln \frac{T_\alpha^2}{\beta} = \frac{E}{RT_\alpha} \quad \ln \beta = -\frac{E}{R} \cdot \frac{1}{T_\alpha} + \text{cte} \quad \ln \frac{T_\alpha}{\beta} = \frac{E}{RT_\alpha} + \ln k_0$$

Experimental Procedure

* Glass Preparation

A mixture of high purity oxides was homogenized and melted in a Pt crucible for 2h at 1600 °C. The melt was poured on a stainless steel plate and immediately splat-cooled with other steel plate, obtaining homogeneous pieces.

| Sample | Chemical Analysis (wt %) | | | |
|--------|-------------------------------|------------------|--------------------------------|--------------------------------|
| | Y ₂ O ₃ | SiO ₂ | Al ₂ O ₃ | Lu ₂ O ₃ |
| YAS | 45 | 35 | 20 | - |
| YAS-Lu | 44.91 | 34.93 | 19.96 | 0.2 |

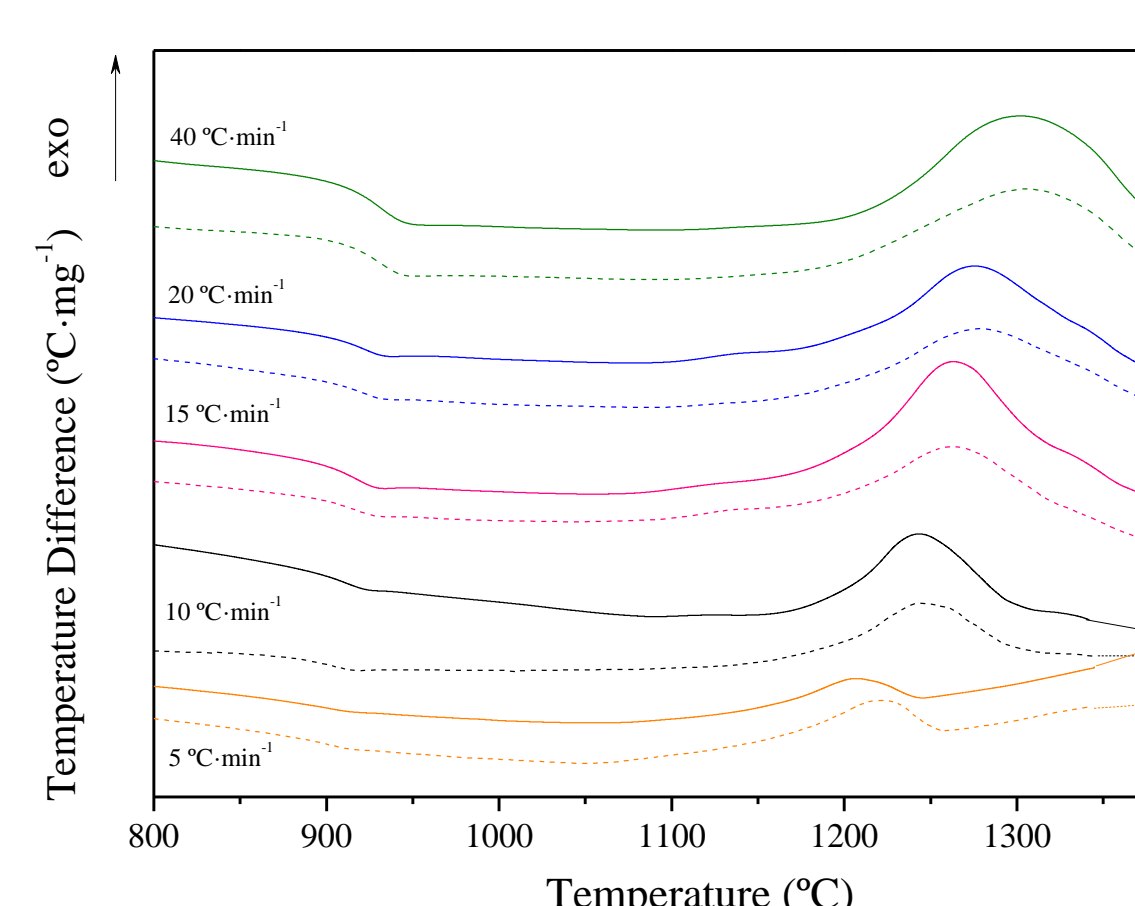
* DTA Non-isothermal measurements

The samples were heated from 25 to 1400 °C, at β : 5, 10, 15, 20 and 40 K·min⁻¹. The thermal parameters determined were: the glass transition (T_g), the onset crystallization (T_c) and the crystallization peak (T_p) temperatures.

Results and Discussion

* DTA measurements of glass slabs

Non-isothermal constant heating rate DTA traces give an overview of the crystallization process of the different glasses at a given heating rate.

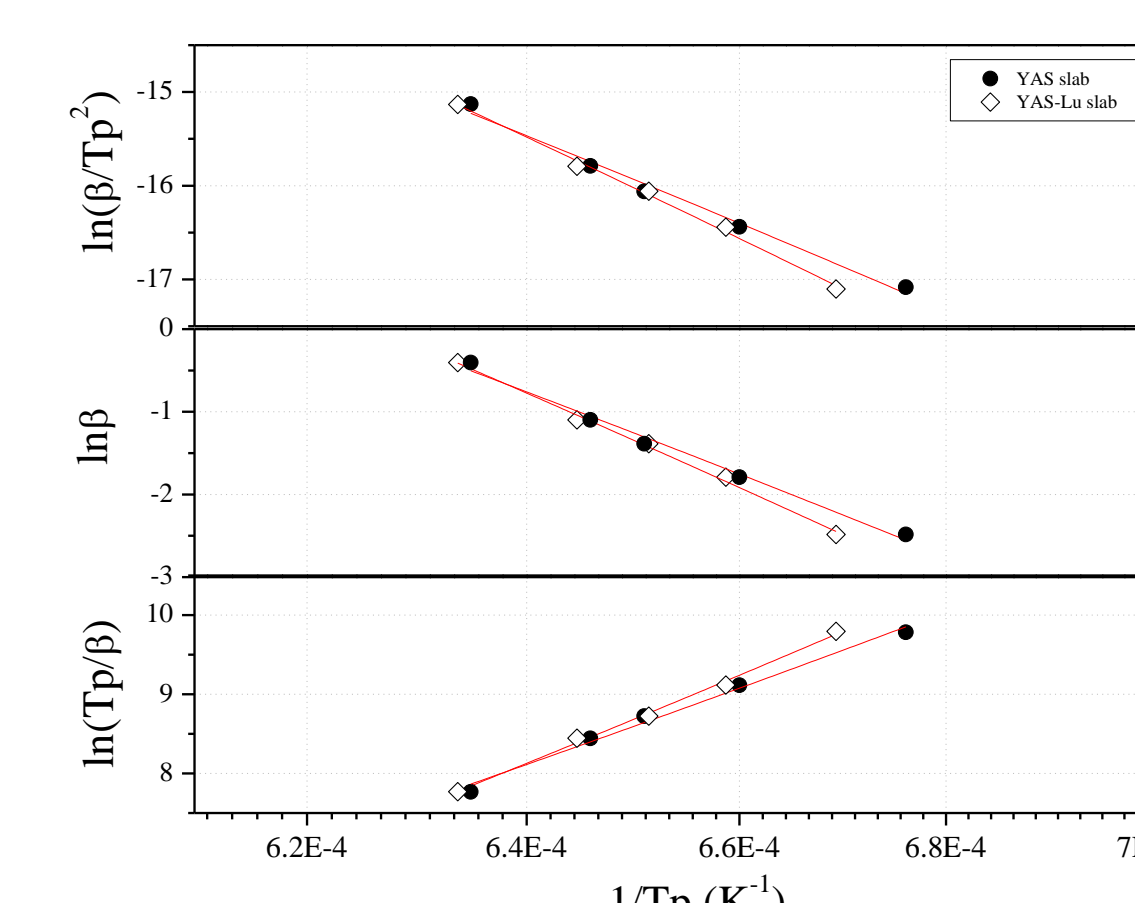


| β (K·min ⁻¹) | YAS | | | YAS-Lu | | |
|-----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | T _g | T _c | T _p | T _g | T _c | T _p |
| 5 | 867 ± 2 | 1072 ± 4 | 1206 ± 3 | 885 ± 2 | 1057 ± 8 | 1221 ± 3 |
| 10 | 895 ± 3 | 1144 ± 6 | 1242 ± 3 | 882 ± 5 | 1082 ± 4 | 1245 ± 4 |
| 15 | 893 ± 5 | 1150 ± 8 | 1263 ± 2 | 900 ± 2 | 1100 ± 6 | 1262 ± 2 |
| 20 | 900 ± 3 | 1162 ± 4 | 1275 ± 3 | 904 ± 2 | 1102 ± 5 | 1278 ± 4 |
| 40 | 908 ± 2 | 1166 ± 5 | 1302 ± 4 | 912 ± 3 | 1122 ± 5 | 1305 ± 3 |

The T_c and T_p are shifted to higher temperatures with increasing heating rates. This means a strong dependence of the exothermic process with the heating rate.

* Overall crystallization energy and Avrami parameter

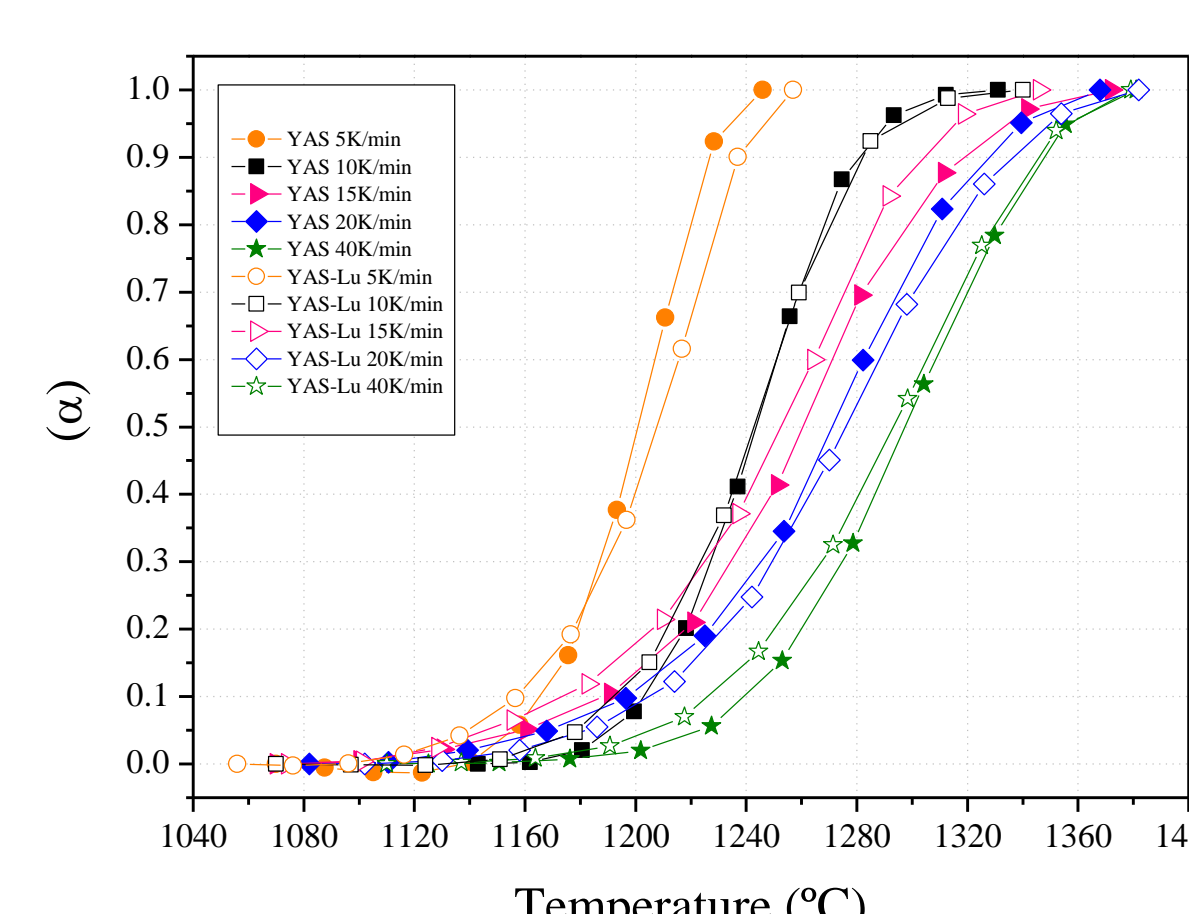
Kissinger, Ozawa and Augis-Bennett methods were used to determine the kinetic parameters from the non-isothermal analysis. The dependence of T_p on the heating rate was described with these methods.



| Method | Sample | Expressions | R | E (kJ/mol) |
|---------------|--------|----------------------------------------------|------|------------|
| Kissinger | YAS | $\ln(\beta/T_p^2) = 14.413 - 46686.8/T_p$ | 0.98 | 389 ± 1.8 |
| | YAS-Lu | $\ln(\beta/T_p^2) = 19.15115 - 54113.49/T_p$ | 0.99 | 450 ± 1.3 |
| Ozawa | YAS | $\ln(\beta) = 31.07281 - 49736.62/T_p$ | 0.98 | 414 ± 1.8 |
| | YAS-Lu | $\ln \beta = 35.82449 - 57184.14/T_p$ | 0.99 | 476 ± 1.3 |
| Augis-Bennett | YAS | $\ln(T_p/\beta) = -22.74291 + 48211.73/T_p$ | 0.98 | 401 ± 1.8 |
| | YAS-Lu | $\ln(T_p/\beta) = -27.4878 + 55648.82/T_p$ | 0.99 | 463 ± 1.3 |

* The crystallized fraction as a function of temperature

Vyazovkin et. al. suggest that the activation energy may vary with α , due to the activation energy of a solid state reaction is generally a composite value determined by the activation energies of several elementary processes.

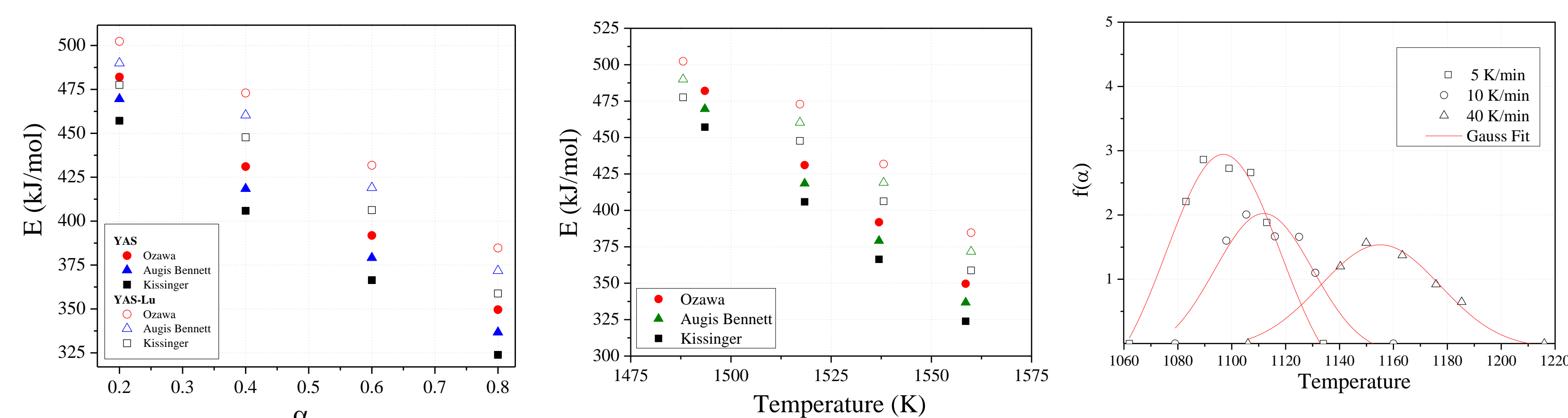


$$m = \frac{2.5 RT_p^2}{E\Delta T}$$

| β (K·min ⁻¹) | YAS | YAS-Lu |
|--------------------------------|-------------|-------------|
| 5 | 0.35 ± 0.01 | 0.31 ± 0.01 |
| 10 | 0.34 ± 0.01 | 0.30 ± 0.03 |
| 15 | 0.34 ± 0.03 | 0.29 ± 0.04 |
| 20 | 0.34 ± 0.02 | 0.30 ± 0.03 |

* Overall crystallization energies at different extent of conversion (α).

The three methods yield a decrease of the activation energy with increasing α .



The activation energy values decrease with temperature suggest that the crystallization rate constant is determined by the kinetics of two processes, nucleation and diffusion. Abdelazim et. al. suggest that due to these mechanisms have different activation energy, the activation energy of the transformation will vary with temperature.

Conclusions

- * The effect of Lu₂O₃ addition on the crystallization kinetics could be determined, as an increase of the activation energy values of about 15% for the isoconversional models used. The higher E values for YAS-Lu glasses, can be related with the lower crystal growth values measured as compared to those measured for YAS glass.
- * Avrami parameter values show also surface crystallization, diffusion limited. The value of this coefficient means that only one dimensional growth can take place.
- * The activation energy shows dependence with α . It was found an almost linear dependence with α for the isoconversional models used.
- * The observed activation energy values decrease with temperatures demonstrates that the rate constant of crystallization is determined by the rates of two processes, nucleation and diffusion. Because these mechanisms are probably to have different activation energies, the effective activation energy of the transformation will vary with temperature. This $k(T)$ increase produces a decrease in $f(\alpha)$. It is found that $f(\alpha)$ fits well a Gauss Ampere function.