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GLASS FORMING ABILITY OF CALCIUM ALUMINOSILICATE MELTS

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Abstract

The glass forming ability (GFA) of two series of calcium aluminosilicate melts is studied by measuring their viscous behavior and crystallization tendency. The first series consists of five compositions on the joining line between the eutectic point of anorthite-wollastonite-tridymite and that of anorthite-wollastonite-gehlenite. The series includes the eutectic compositions as end members. The second series consists of five compositions on a line parallel to the joining line on the alumina rich side. In the present work, GFA is described in terms of glass stability, i.e. the ability of a glass to resist crystallization during heating. In addition, the fragility index (m) is derived by fitting the viscosity data with the Avramov-Milchev equation. The results show that m is inversely proportional to the glass stability for the two series of melts, implying that m is an indirect measure of GFA. However, this proportionality is only valid for comparison of the glasses in the same series of compositions. The eutectic composition of anorthite-wollastonite-tridymite is found to exhibit the highest GFA of the melts under investigation.

Keywords: Calcium aluminosilicates, viscosity, fragility, glass stability, glass forming ability

Introduction

Nowadays inorganic glasses can be made in many ways, e.g. by chemical vapor deposition, solid-state reactions and sol-gel methods. However, the predominant way for producing inorganic glasses is still the melt-quench process. To optimize this process for producing high quality glasses, it is essential to know the glass forming ability (GFA) of a given melt. From a kinetic point of view, any melt can be made glassy if the quenching process is sufficiently fast to avoid crystallization. The critical cooling rate is the minimum rate required to vitrify a melt. This rate can be considered as a direct measure of GFA [1,2]. However, determination of the critical cooling rate is not always an easy task. Therefore it is of special interest for glass scientists to seek alternative methods for determining GFA.

The objectives of this work are to define and quantify GFA of ten calcium aluminosilicate (CAS) melts by determining the stability of the formed glasses upon reheating. This stability refers to the ability of a glass to bypass crystallization

upon heating. In this work the Hruby parameter (K_H) obtained from calorimetric data is used as a measure of glass stability (Eq. 1) [3]. In Eq. 1 T_g is the glass transition temperature, T_c the onset temperature of crystallization, and T_m the melting temperature.

$$K_H = \frac{T_c - T_g}{T_m - T_g} \quad (1)$$

The larger the parameter K_H , the higher is the glass stability. Since an inverse linear relation is found between K_H and the critical cooling rate, K_H may be used as a measure of GFA of a melt upon cooling [3-5].

The temperature (T) dependences of viscosity (η) are measured using viscometry and described by the Avramov-Milchev (AM) equation:

$$\log \eta = \log \eta_\infty + (12 - \log \eta_\infty) \left(\frac{T}{T_g} \right)^F \quad (2)$$

where η_∞ is the viscosity at infinite high temperature, and F is the fragility index [6].

In addition to the fragility parameter F derived from the AM equation, Angell and co-workers [13,14] have proposed another fragility index (m) defined as the slope of the fragility plot, i.e. the $\log \eta$ versus T_g/T plot, at T_g . From Eq. (2) and the definition of m , F can be linked to m in the following manner [15]:

$$m = (12 - \log \eta_\infty)F. \quad (3)$$

It is noticed that for determining m the parameter $\log \eta_\infty$ is taken into consideration. In general $\log \eta_\infty$ is for the ten melts observed to decrease with increasing values of NBO/T. An inverse correlation between fragility and GFA has been found for various metallic glasses [7-9], and hence, fragility can be used as an alternative measure of GFA for those systems. Now the question is whether this is the case for the CAS system. In this work we clarify this question by determining the Hruby parameter and the fragility of two series of CAS glass compositions.

Two series of five compositions each were synthesized and investigated in this work. The eutectic series (CAS1 to -5) is positioned on the joining line connecting the two eutectic compositions of anorthite-wollastonite-tridymite (An-Wo-Tri) and anorthite-wollastonite-gehlenite with the two eutectic compositions being the end members. The non-eutectic series (CAS6 to -10) is positioned parallel to the

eutectic series at larger alumina concentrations. The chemical compositions are seen in Table 1. The table also states the number of non-bridging oxygen per tetrahedron (NBO/T) for each glass.

Table 1: The compositions (in mol%) of the 10 CAS melts found by means of wet chemistry:

	SiO ₂	Al ₂ O ₃	CaO	NBO/T
Eutectic series	CAS1	64.9	9.3	25.8
	CAS2	59.9	10.0	30.1
	CAS3	54.7	10.9	34.4
	CAS4	49.6	11.7	38.7
	CAS5	44.4	12.5	43.1
Non-eutectic series	CAS6	61.6	14.9	23.4
	CAS7	57.8	15.8	26.3
	CAS8	51.9	16.8	31.3
	CAS9	48.1	18.9	33.0
	CAS10	42.7	19.3	38.0

In the low viscosity range (approx. 10^0 - 10^3 Pa s) the viscosity was measured using concentric cylinder viscometry, and in the high viscosity range (approx. 10^8 - 10^{13} Pa s) the viscosity was measured by means of micro penetration viscometry using a vertical dilatometer. T_g and T_c were measured using differential scanning calorimetry (DSC) by heating the samples up to 1723 K at a heating rate of 20 K/min. The heat capacity curves were obtained using the evaluation method described in [10,11]. Further details about the experimental work including the production process of the ten glasses can be found in [12].

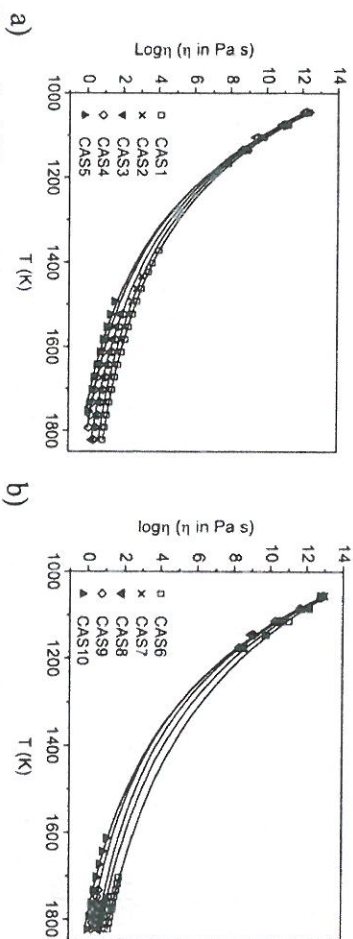


Figure 1. a) Viscosity (η) given as $\log \eta$ as a function of temperature (T) for the ten melts. The symbols are the measured values and the lines are obtained by fitting the AM equation to the viscosity data.

Figs. 1a and b show the obtained viscosity data as well as the fit of the equation (Eq. (2)) to the data. From the figure it is observed that the AM equation provides a rather good description of the data ($R^2 > 0.999$). F can be obtained from the AM fit and m is found using Eq. 3 (Table 2). As expected, the fragility increases with increasing NBO/T within each series.

Table 2. Properties of the 10 CAS melts. F is obtained from fits of the AM equation viscosity data. m is found from Eq. 3. T_g and T_c are found from DSC using a heating rate of 20 K/min. T_m is found using the model proposed by [16] and K_{II} is the Hruby parameter defined in Eq. 1.

	F (-)	m (-)	T_g (K)	T_c (K)	T_m (K)
Eutectic series	CAS1	3.74 ± 0.05	47.5 ± 0.6	1070	1443
	CAS2	3.7 ± 0.1	48 ± 1	1062	1543
	CAS3	3.7 ± 0.1	50 ± 1	1063	1554
	CAS4	3.8 ± 0.1	52 ± 1	1064	1562
	CAS5	3.8 ± 0.2	53 ± 3	1068	1538
Non-eutectic series	CAS6	2.9 ± 0.2	40 ± 3	1106	1379
	CAS7	3.2 ± 0.1	44 ± 1	1091	1330
	CAS8	3.6 ± 0.3	48 ± 4	1080	1320
	CAS9	3.69 ± 0.09	51 ± 1	1096	1332
	CAS10	3.4 ± 0.2	49 ± 3	1095	1347

Figs. 2a and b depict the temperature dependence of isobaric heat capacity (C_p) obtained for the glasses in the eutectic and non-eutectic series, respectively. It is seen that no crystallization is observed for CAS1 and -2.

T_g and T_c are found from the calorimetric measurements (Table 2) estimated based on the model proposed in [16]. This model assumes that the values obtained for K_{II} of stable glasses having a low tendency to crystallize. This is due to the fact that crystallization can be bypassed when glasses are heated at a normal rate of e.g. 20 K/min. Therefore, T_c is not determined and hence K_{II} can not be determined. This behavior is observed for CAS1 ;

As DSC is a dynamic method, the characteristic temperatures of the transitions are dependent on the heating rate employed during the measurement. Thus, the values obtained for K_{II} depend on the heating rate. This dependence rises to difficulties in obtaining K_{II} of stable glasses having a low tendency to crystallize. This is due to the fact that crystallization can be bypassed when glasses are heated at a normal rate of e.g. 20 K/min. Therefore, T_c is not determined and hence K_{II} can not be determined. This behavior is observed for CAS1 ;

Thus, K_H may only be used for quantifying the GFA of glasses with a relative high tendency to crystallize.

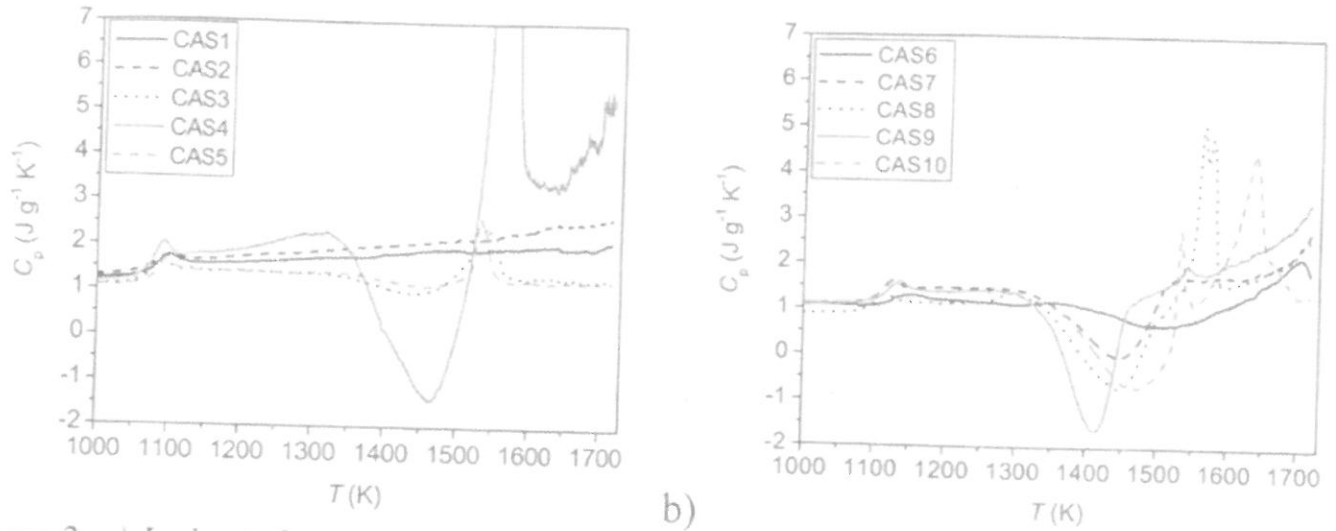


Figure 2. a) Isobaric heat capacity (C_p) versus temperature (T) for the ten glasses. All DSC measurements were carried out in atmospheric air at a heating rate of 20K/min.

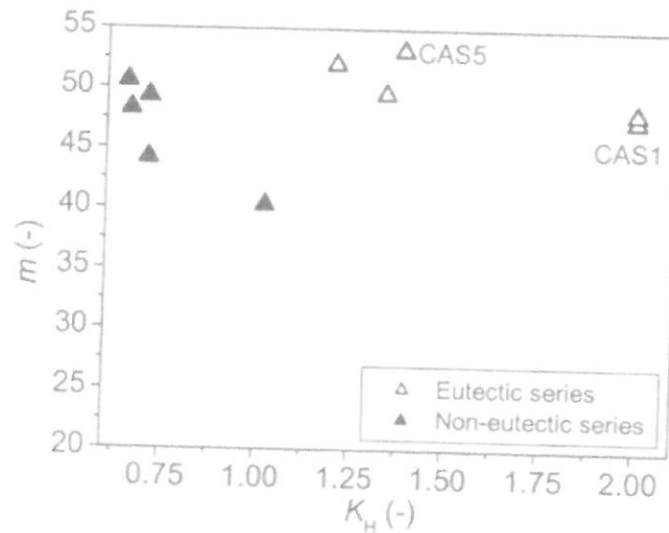


Figure 3. The fragility index (m) as a function of the Hruby parameter (K_H) for the ten compositions.

To test whether the inverse correlation between fragility and K_H exists for the CAS melts examined in this work the values of m and K_H are compared in Fig 3. Within each series, m is observed to decrease with K_H . This trend is most obvious for the non-eutectic series. For CAS1 and -2, K_H is set to be 2 to reflect the highest stability of these two glasses upon reheating [3]. Therefore it can be stated that an inverse correlation between fragility and GFA exists within a series of CAS melts with systematic compositional variations.

Conclusions

In summary, GFA of ten CAS melts has been quantified by the glass stability, while the fragility of these melts has been determined by fitting the AM

equation to viscosity data. An inverse correlation between fragility and GFA is found for the same series of peralkaline CAS melts with systematic compositional variations. In detail, the stronger the glass melt, the higher is its GFA. In overall, the five eutectic compositions exhibit higher GFA than the five non-eutectic ones. CAS1 possesses the highest GFA of the ten melts.

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