



Liquidus temperatures of calcium magnesium aluminosilicate glass-forming compositions determined via gradient furnace and from the melting peak by differential thermal analysis



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ABSTRACT

The liquidus temperatures (T_L) of good glass forming systems within the CaO–SiO₂–MgO–Al₂O₃ system (CMAS) were evaluated. The determination of T_L via differential thermal analysis (DTA) was studied in terms of reproducibility and was compared with results from the gradient furnace method. Seventeen different glass compositions within the CaO–SiO₂–MgO–Al₂O₃ system were melted from technical raw materials. Since those glasses are reluctant to crystallize, a prior heat treatment was necessary to induce crystallization. The onset and the endpoint of the melting peaks of pre-crystallized materials were measured with a heating rate of 2 K/min and compared with the liquidus temperatures obtained by the gradient furnace method (following the ASTM standard procedure C 829-81 [11]). The endpoint temperatures of the melting peaks were closest to the results determined via the ASTM procedure. Most endpoint results via DTA differ by not more than 10 K compared to the liquidus temperatures. Because of the simultaneous crystallization pretreatment of many different compositions, the small amount of glass needed, and the speed of the DTA, this technique may be a valuable option to estimate the liquidus temperature of complex multicomponent glasses.

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1. Introduction

The liquidus temperature, T_L , is a very important parameter in the glass production industry since in an industrial glass melt for commercial products, crystallization should not occur within the temperature range used for forming the glass, especially glass fibres [2,3]. The liquidus temperature is defined as the highest temperature at which crystals are thermodynamically stable in contact with the melt; both the liquid and the solid state are in equilibrium at this temperature and all crystals dissolve above it [3–5]. In multicomponent glass forming systems, below T_L , crystals form within a few hours and remain in equilibrium with the liquid [6]. The accurate knowledge of T_L is hence crucial to the effectiveness of the production process of glasses, because it affects the workability of the glass melt in case of temperature fluctuations below T_L which might induce devitrification. Thus also the production costs are affected since T_L generally provides a clear indication of the minimum possible melting and forming temperature [7]. Especially in

multicomponent systems, small compositional changes can cause dramatic changes in the liquidus temperature [6,8,9].

The ternary systems MgO–Al₂O₃–SiO₂ and CaO–Al₂O₃–SiO₂ with minor additions of different network modifiers have been extensively studied for possible use in dentistry [10], hard disc substrates [11,12], laser applications [13] and fibreglass [14,15], for example.

The quaternary glass forming system CaO–MgO–Al₂O₃–SiO₂ (CMAS) is particularly interesting, because of its inexpensive raw materials, its high corrosion resistance and good mechanical properties and received quite some attention [1,16–22]. It is now commonly used for boron free fibre glass production to meet industry requirements [14,19,23,24]. However, thermodynamic data are often not available and while some thermodynamic models can accurately reproduce binary phase diagrams, their ability to predict multicomponent properties based on information from the existing binary systems is much more limited, especially in the presence of MgO [17]. Furthermore, it is difficult to extrapolate empirical models out of range of previous experiments; the accuracy of some model calculations of multicomponent systems can be quite low even just outside the assessed composition area [17]. Therefore, for good glass forming systems, T_L as a function

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Table 1
Normalized XRF – compositions of the studied glasses (wt%).

	SiO ₂	Al ₂ O ₃	CaO	MgO	ZnO
1	60.65	14.85	12.82	10.45	1.23
2	59.95	14.86	12.83	11.21	1.14
3	59.07	15.72	12.52	11.61	1.08
4	60.27	14.52	12.52	11.61	1.08
5	59.01	14.50	13.70	11.60	1.18
6	61.68	14.49	12.50	10.10	1.24
7	59.63	15.21	13.14	10.81	1.21
8	58.82	14.46	15.15	10.07	1.50
9	59.06	16.02	12.51	11.31	1.11
10	59.34	15.61	12.82	11.06	1.16
11	59.90	15.60	12.82	10.45	1.23
12	59.23	14.83	14.15	10.44	1.35
13	59.27	15.59	13.41	10.45	1.28
14	60.18	15.99	12.50	10.10	1.24
15	59.32	14.86	13.42	11.21	1.20
16	59.35	15.46	12.83	11.21	1.14
17	58.91	15.98	13.68	10.08	1.35

of composition is usually determined experimentally, despite the fact that this is costly and time consuming [5,17].

The traditional procedure to obtain T_L involves promotion of crystallization in glass samples at different temperatures and evaluation using a microscope either simultaneously or subsequently [5,25,26]. This so called ‘uniform temperature method’ can be accelerated using a gradient temperature furnace following the ASTM-Standard C829 [1]. The reliability of those methods is highly dependent on the experience and the eye of the operator and his or her interpretation. Another difficulty is the fact, that in most cases slowly crystallizing glasses are desired for the commercial glass products such as fibres [14]. Hence, the determination of the liquidus temperature can be effortful, inexact and time consuming. The statistical error distribution of the used gradient furnace with 20 tests of the same glass was ± 7 K. Beerkens and Conradt [4] reported that the investigation of one glass sample in 6 different laboratories gave variations of 50–60 K.

Therefore another method using differential thermal analysis (DTA) has also been tested for glasses with stoichiometric compositions and one multicomponent system by Ferreira et al. [5]. It has been reported in several papers [5,27–29] that the endpoint of the melting reaction for binary systems should be used as equivalent for T_L . Also it is very important to use a very small heating rate to prevent the overrunning of effects such as melting [5].

This paper presents a study on the liquidus temperatures of the quaternary CMAS system. The characteristic temperatures of the melting peaks determined on heating by DTA of glasses pretreated for crystallization were compared with the results of the liquidus temperatures measured by a gradient furnace.

2. Experimental procedure

For this work 17 glass compositions in the quaternary system CaO–SiO₂–MgO–Al₂O₃ were used. The samples were in the following wt% composition range: 58.82–61.68 SiO₂, 14.46–16.02 Al₂O₃, 12.5–15.15 CaO, 10.07–11.61 MgO, and 1.08–1.50 ZnO (Table 1). ZnO was included in the compositions in order to study the effect on the crystallization temperature [30]. Seventeen different glass compositions within these limits were melted using technical raw materials with less than 1 wt% of impurities.

The glasses were prepared from 25 g batches from the following ground raw materials in industrial quality: burnt lime, kaolin, fine quartz, dolomite, magnesium oxide and calcined alumina. They were mixed and melted in a platinum crucible at 1500 °C for 3 h. After fining, the melts were cast into graphite moulds.

For the determination of T_L , crushed glass with a grain size smaller than 850 μm was put into a platinum boat. The platinum

boat was placed into an Orton tubular furnace with 8 thermo couples for temperature observation and preconditioned at 1500 °C for 1 h. Afterwards the melt was exposed to a certain preset temperature profile for crystallization in the gradient furnace for 24 h. It was subsequently studied using an optical microscope. The position in the boat where the first crystals appear, going from high to low temperatures, was determined. This position is attributed to a certain temperature in the gradient temperature furnace which corresponds to T_L .

Differential thermal analysis or DTA is a dynamic measuring system, which is obviously not very suitable for slowly crystallizing glasses as fibre glasses. Hence a pre-crystallization step is necessary. Then the pre-crystallized material is heated up to melt in the DTA. After a series of tests, the following measuring procedure was chosen.

Glass powder with a grain size of 40–100 μm was prepared in order to maximize the surface area in order to make use of surface crystallization. To guarantee a large number of crystals in the sample, a nucleation step had also been added to the pre-crystallization process. To nucleate the glasses, the powders were kept at temperatures which were 30 K above their glass transition temperatures (around 770 °C) for 8 h and subsequently heat treated at a temperature close below the estimated liquidus temperature for 24 h. This was done to ensure a growth of the primary crystal phase in the glass [31,32]. This two-step heat-treatment was performed on a platinum–gold alloy mould in a superkanthal furnace. In this case, all glasses were crystallized at 1100 °C for better comparability.

The partially crystalline specimen was again manually crushed and powdered with a mortar to a grain size of 25–40 μm. This small grain size was chosen in order to minimize effects due to the temperature gradient of larger grains. In a test run with monolithic glass ceramic pieces, the endpoint of the DTA melting peak shifted more than 50 K to higher temperatures compared to that from a powder sample.

The DTA analyses were carried out with a Shimadzu DTA 50 and a Netzsch STA 429. The heating rate was chosen to be as low as 2 K/min within the interesting temperature range from 1000 to 1300 °C to prevent the overrunning of effects. In preliminary tests, a higher heating rate of 10 K/min showed a temperature shift of at least 10 K to higher endpoint temperatures. Then the DTA curves were evaluated with the ‘tangent method’ provided by the analysis software of the Shimadzu DTA used. Hereby the intersection of the tangent to the curve, traced to the baseline and on the side of the peak is used.

The glasses were studied by a polarizing microscope Leitz LaborLux 12 POL and by X-ray fluorescence (XRF) using a PANalytical MagixPro (4 kW Rh Tube).

For validation of the methods two commercial glasses HiPer-tex™ and Advantex® (the latter is a trademark of Owens Corning used under license) were chosen as calibration standards.

3. Results and discussion

Our chosen calibration glasses HiPer-tex™ and Advantex® showed – in agreement with [5,27–29] – that the endpoint is the best measure for the determination of the liquidus temperature. The liquidus temperature assessed with the tube furnace is similar to the melting peak endpoints of both Advantex® and HiPer-tex™.

As shown in Fig. 1, the different test runs of the DTA curves of HiPer-tex™ are quite similar. The powdered glass samples were nucleated at either 800 °C or 900 °C and crystallized at 1000 °C, 1150 °C, or 1200 °C to test the effect of the crystallization temperature. Two measurements of each set were done to test the effect of heating rate (the black curve was recorded using 5 K/min) and the

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