Glass transition temperature and activation energy of sintering by optical dilatometry

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ABSTRACT

A new possibility for measurements of glass transition point, fictive temperature and activation energy of viscous flow in the glass transition range is shown by using a contactless horizontal optical dilatometer and pressed powder samples. The results are compared with ones, obtained with bulk samples and traditional differential contact dilatometer. The possibility for a correct measurement of the activation energy of sintering, E_{sin}, is also highlighted by means of glasses with different compositions and various crystallization trends. In glasses with low crystallization trend E_{sin} decreases with the temperature rise in the whole sintering range; in glasses with higher crystallization ability, E_{sin}, starts anomaly to increase with the beginning of the phase formation. As a result, at low heating rates the densification is partially inhibited.

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1. Introduction

The viscosity variations of glass forming melts vs. temperature have fundamental significance for the glass science and industry. In order to characterise this viscosity–temperature curve a number of specific viscosity values are selected as reference points [1–5]. These particular viscosities are chosen due to their significance in various aspects of the industrial and laboratory processing.

Since the viscosity of glass forming melts vary by 12–13 orders of magnitude between the strain point and the melting point its measurements require the usage of different techniques, each of which is restricted to a limited range of viscosity values [1–5] and sometime requires specific sample preparation. In addition, when nucleation and crystallisation or liquid–liquid immiscibility takes place during the measurement an increasing of the viscosity might be observed [1,6,7], which compromise the obtained results.

Most interesting are the viscosity changes in the glass-transition range, where the glass transition temperature, T_g, is the most discussed and studied characteristic temperature. However, despite of its importance, the methods for determination of T_g are not yet unified in the glass society [1,8].

In a big part of technical literature T_g is associated with viscosity of 10^{13} dPa s or $10^{13.3}$ dPa s and its measurements usually is related to DSC or dilatometric measurements [1–3,8,9]. In the case of evaluation by dilatometry well annealed monolithic bulk samples are heated at 3–5 K/min and T_g is acquired as the onset from the kink in experimental curve; the error in this kind of measurements is estimated as ±2 to 3 K. For example, Vogel suggest to measure the glass transition point after cooling of the sample at 1 K/min thought the glass transition region and subsequent heating at 5 K/min [3]. Similar are also the standards, used in "Experimental Glass Station"- Murano (Venice) [5].

The variations of properties and structure in the glass transition region depend not only on the thermal history, but also on the direction of heat-treatment (i.e. heating or cooling). Thus, in order to distinguish the differences, observed at heating and at cooling, the idea for fictive temperature, T_f, has been introduced [8,10,11]. According this statement T_g is measured on slow cooling, while the corresponding temperature, measured on heating, is defined as T_f. Practically, T_g is the temperature at which the extrapolated lines of non-stable solid glass and meta-stable liquid cross, while T_f is the temperature at which the fixed glassy structure will be in an equilibrium. In principle, T_f can be estimated at a temperature slightly lower than T_g, but in many cases the differences is comparable with the experimental error in the dilatometric measurements [8,10].

Although T_g can be measured correctly only on cooling, it often continue to be measured on heating due to difficulties to control a constant cooling rate (especially in the dilatometric experiments). In addition, the condition for slow cooling cannot be respected when the studied composition is characterised by high trends of liquid–liquid immiscibility or/and crystallisation. In these cases, instead slow cooling of the samples an annealing treatment at temperature lower than T_g, seems to be more appropriated.

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Table 1
Chemical compositions (wt %) of the used glasses.

	CG	G	WG	MG
SiO_2	72.0	71.4	49.8	57.7
Al_2O_3	0.2	0.6	11.1	–
B_2O_3	–	–	–	5
Fe_2O_3	0.2	0.1	4.5	–
CaO	10.1	9.8	19.5	18
$CaF2$	–	-	–	2.8
MgO	2.8	3.3	4.0	14.4
Na_2O	13.9	13.3	5.0	2.2
K_2O	0.7	1.3	1.8	–
P_2O_5	–	–	1.9	–
Others	–	–	1.4	2.7

The dilatometric measurements have traditionally been performed using monolithic samples and push rod dilatometer. In order to obtain highly reliable results in measurements above the glass-transition range (with a minimum effect associated with the viscous deformation of samples), it is necessary to use a dilatometer with a weak measuring force and samples with a large cross-sectional area, so that the measuring pressure is kept at low values. A recent innovation in the field of dilatometry is the chance to carry out measurement of the dimensional variations without touching the sample, but simply by observing its two tips with two high-definition cameras [12]. This new equipment gives results, somewhat similar to ones obtained by the widely used hot stage microscopy [13–15], but the accuracy of the measurements is considerably higher.

This contactless dilatometric measurement allows to widen the application fields of the traditional contact technique and gives advantages in terms of sample preparation (i.e. monolithic samples with different size can be investigated, as well as pressed powders). It is very important also that, from an instrumental point of view, the thermal shift between purely elastic behaving to visco-elastic does not represent an actual limitation for the acquisition of dilatometric data. As a result, it becomes possible to realize also tests on samples with a fully viscous behaviour. In this manner it is possible to study correctly the kinetics of sintering processes driven by viscous flow, as well as to evaluate the actual influence of crystallisation on the densification process in the production of sintered glass-ceramics.

In the present work some detail for these new possibilities are highlighted and discussed.

2. Experiments

Four glasses having different crystallization abilities, whose chemical compositions are summarized in Table 1, were used. The first composition (labelled CG) and the second composition (labelled G) are similar compositions for container uncoloured glass and window glass, respectively, which was washed, crashed and milled below 71 μm. The third glass (labelled WG) comes from as-it-is vitrification (i.e. without additives) of bottom ashes from Municipal Solid Waste Incinerator [16]. The fourth composition (labelled MG) is a model glass, which was melted at 1400 °C for 1 h and then instantly quenched in water. The WG and MG frits also were milled bellow 71 μm.

The crystallization trends of obtained glass powders were investigated by DTA (PerkinElmer Diamond apparatus) at heating rate of 20 °C/min and using samples of ∼20 mg.

The glass powders were mixed with a 7% PVA solution, unaxially pressed with pneumatic press "Nannetti" at 40 MPa into "greens" with size $50 \times 5 \times 3$–$4 \, mm^3$ which after that were dried at room

temperature. The initial total porosities, P_T, of the samples (for series of 5 specimens) were estimated by the relationship:

$$P_T = 100 \times \frac{\rho_{as} - \rho_a}{\rho_{as}} \qquad (1)$$

where ρ_a is apparent density and ρ_{as} is absolute density. ρ_a was calculated by measuring samples volume with precise electron micrometre, while ρ_{as} – using the initial glass powders and argon displacement Pycnometer (AccuPyc 1330).

After preliminary 30 min step at 280 °C (in order to eliminate the PVA binder) the samples were heat-treated in optical dilatometer "MISURA HSML-ODLT 1400" at different heating rates up to 1000 °C or to temperatures, where deformation of the sintered samples starts.

The results, obtained with CG glass, were compared with earlier data from analogous composition acquired with contact differential dilatometer "Netzsch 402 ED" [17]. In this previous work bulk and pressed powder samples of container glass were heat-treated at different heating rates in order to evaluate the glass transition range, the activation energy of viscous flow in the glass transition range, E_{Tg}, and the activation energy of sintering E_{sin} at different shrinkage values.

The activation energies of sintering can be estimated by the Cheng equation [17–19]:

$$\ln\left(\frac{v}{T_x^2}\right) = -\frac{E}{RT_x} \qquad (2)$$

where T_x are temperatures corresponding to a fixed degree of transformation (in the case of sintering – equal percentages of shrinkage) obtained at different heating rates v. The plot of $\ln(v/T_x^2)$ versus $1/T_x$ is a line, whose slope corresponds to the activation energy.

Similar relationship (i.e. the Kissinger equation) is widely applied to study the phase transformation in glasses and other solids by DTA or DSC [19–21]. In the Kissinger equation T_x corresponds to the temperature of maximum transformation rate, T_p, which at non-isothermal crystallisation always is related to the degree of transformation $\alpha \sim 0.61$ [22] (i.e. in this case the equations of Cheng and Kissinger coincide). However when the degrees of transformation, reached at T_p, vary with the heating rate (which is possible in some cases of sinter-crystallization) both equations give different results.

Eq. (2) was also used for the evaluation of activation energy of viscous flow in the glass transition range, E_{Tg}. It can be noted that the results, obtained with the Cheng equation, are very similar also to ones, calculated with the widely used relationship of Bartenev [22].

3. Results and discussion

3.1. Accuracy and reproducibility of results, obtained with optical dilatometer

The work principle of the double beam optical dilatometer is direct vision of both the tip of specimen captured by two digital camera equipped with high magnification and long working distance optical systems and controlled by a micrometric slide. Since it is not possible to push the optical magnification beyond the wavelength of light, the maximum resolution of the optical system can be slightly higher than the wavelength of light. In the equipment used for this research work the resolution is 0.5 micron per pixel.

The horizontal optical dilatometer utilized in this work, uses ∼50 mm long sample, displaced horizontally into the furnace and lighted by two beams of blue light with a wavelength of 478 nanometers. Two digital cameras capture the images of the last few hundreds microns of each sample tip. Measuring both ends of the
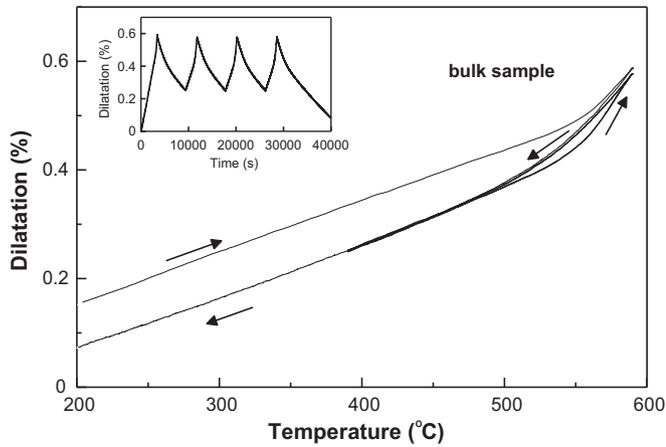
Fig. 1. Dilatometric traces of continuous experiment with optical dilatometer and bulk window glass sample in the glass transition range (heating rate of 5 °C/min and cooling rate of 2 °C/min).
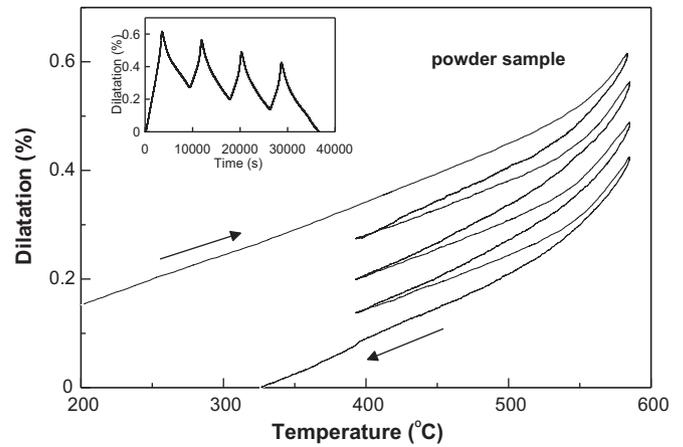

Fig. 2. Dilatometric traces of continuous experiment with optical dilatometer and window glass powder compact in the glass transition range (heating rate of 5 °C/min and cooling rate of 2 °C/min).

specimen with two beams of light at the same time without making contact, it provides an absolute "in situ" measurement. Using a specimen with a total length of 50 mm the precision is of one part over 100,000.

Even though the resolution is lower than push rod dilatometers or interferometers, the elimination of any pressure on the specimen broadens the range of possibilities of measurement thermo-mechanical behaviours up to a temperature range where the material behave in a visco-elastic manner. The curves obtained on solid glass specimens resemble the curves obtained with a mechanical dilatometer. The difference is that the shortening of the sample after reaching the maximum expansion is only given by surface tension, which, thanks to the lowering of viscosity, becomes able to round the tip of the specimen. This feature makes it possible to measure the sintering behaviour on glass powder compacts, which is unfeasible on pushrod dilatometers and is not satisfactory on single optic traditional heating microscopes, because of a much lower resolution of the image. Practically, to reach the same resolution on a heating miscroscope it would be necessary to use a camera with 10^5 pixel in line.

In order to demonstrate the reproducibly of the results, obtained with optical dilatometer, two continuous experiments were made using bulk and pressed powder samples from window glass (G). The bulk sample (with size $50 \times 5 \times 3$ mm^3) was obtained after cutting and polishing, while the powder sample was prepared according to the procedure described in the experimental part. Both samples were heat treated with heating rate of 5 °C/min up to 580 °C and then cooled at 2 °C/min to 400 °C [8]. After that 3 identical cycles of heating with 5 °C/min and cooling with 2 °C/min were carries out in the temperature interval 400–580 °C. The obtained dilatometric results as function of the temperature are shown in Figs. 1 and 2 for bulk and powder samples, respectively; dilatations vs. time are presented in the corresponding insets.

Fig. 1 demonstrates that during the first run of heating and cooling some annealing carries out and as a result the curve, obtained on cooling is bellow one, obtained on heating. However, during the subsequent three runs the curves on heating and on cooling overlaps entirely, which demonstrate a very good reproducibility. T_f at heating with 5 °C/min was evaluated at 551 ± 2 °C, while T_g at cooling with 2 °C/min was evaluated at 544 ± 2 °C.

The results with pressed powder sample (Fig. 2) show similar results, but highlight small densifications during each of the runs (at about 0.1% shrinkage). This phenomenon probably might be explained by a negligible sintering or by smoothing of the pressed grains. Notwithstanding of the observed "creep" T_g and T_f

temperatures, measured during all 4 runs, vary within ± 3 °C and are comparable to ones, observed with the bulk sample.

3.2. Evaluation of glass transition temperature, fictive temperature and activation energy of viscous flow in the glass-transition range

Fig. 3 presents dilatometric traces in the glass transition range of CG glass, obtained with a contact dilatometer at heating with 5 °C/min using bulk and pressed powder samples [17]. The curve of the bulk sample shows fictive temperature at 561 ± 2 °C and dilatometric softening point at 615 ± 2 °C, which is a typical performance for this composition [2,5]. However, when powder sample is investigated with contact dilatometer the both characteristic temperatures cannot be identified due to the "push rod" pressure, applied on the sample.

Fig. 4 shows traces of pressed CG powder sample, studied with optical dilatometer at heating rate of 5 °C/min up to 600 °C, 5 min holding and cooling at 5 °C/min. This experiment was repeated with the same sample 5 times in 5 different days and the obtained results highlight identical accuracy as one of the experiment with the continuous heating and cooling (see Fig. 2). The average values of T_f and T_g from this series of 5 experiments were estimated as 557 ± 2 °C and 560 ± 3 °C, respectively.
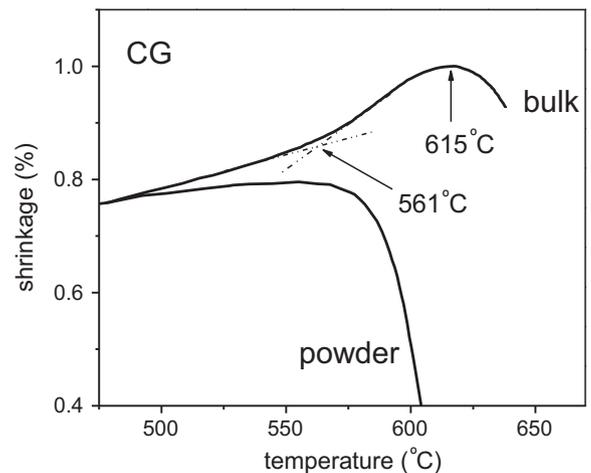

Fig. 3. Dilatometric traces with contact dilatometer in the glass transition range for bulk sample and pressed powder compact of CG glass at heating rate of 5 °C/min [17].
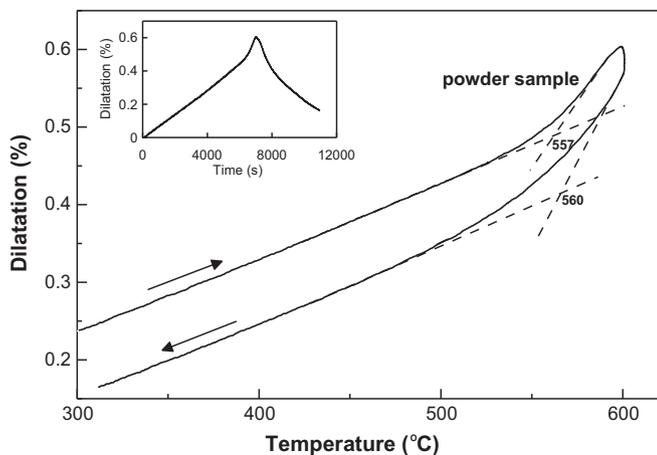
Fig. 4. Dilatometric traces with optical dilatometer and CG glass powder compact in the glass transition range at heating and cooling rates of 5 °C/min.

Fig. 6. Dilatometric traces in the glass transition range of WG glass powder compacts, obtained at different heating rates.

Fig. 7. Dilatometric traces in the glass transition range of MG glass powder compacts, obtained at different heating rates (solid lines – annealed glass powders; traced lines - quenched glass powders).

The made experiments with window and container glass powders expand the application range of optical dilatometry in the glass transition range. It is highlighted that the results, obtained with pressed powders and optical dilatometer, are comparable to ones of bulk samples, investigated with contact or optical dilatometers.

The activation energy of viscous flow in the glass transition range, E_{Tg}, can be evaluated by Eq. (2) using data obtained at different heating rates. Usually, these results are acquired with DTA or DSC, as well as with contact dilatometer and bulk glass samples. In this study for first time is demonstrated that similar data can be correctly obtained also by using pressed glass powder and optical dilatometer.

The dilatometric traces at different heating rates of CG, WG and MG glass powders compacts are presented in Figs. 5, 6 and 7, respectively. The CG and WG samples demonstrate an ordinary behaviour, typical for annealed glasses, and the T_f variations correspond to E_{Tg} of 585 kJ/mol for CG and 887 kJ/mol for WG (Fig. 8). These values are in a good agreement with the data, obtained for similar compositions with other techniques [2,5,23].

Due to the high quenching rate, the initial MG glass powders show results (presented with traced lines in Fig. 7), which are typical for un-annealed glasses [1,9] and demonstrate some densification after the region of strain point temperature. For this reason additional experiments were made, using preliminary annealed for
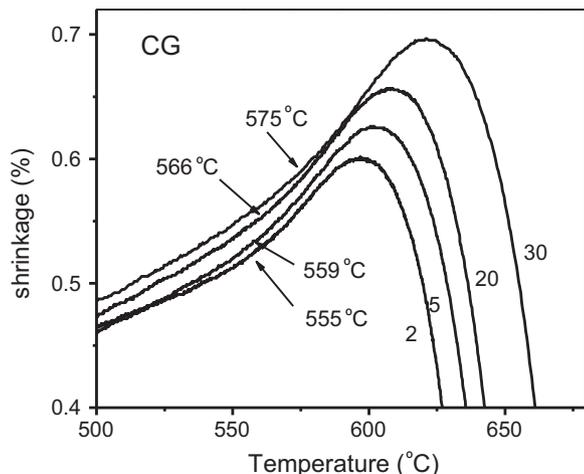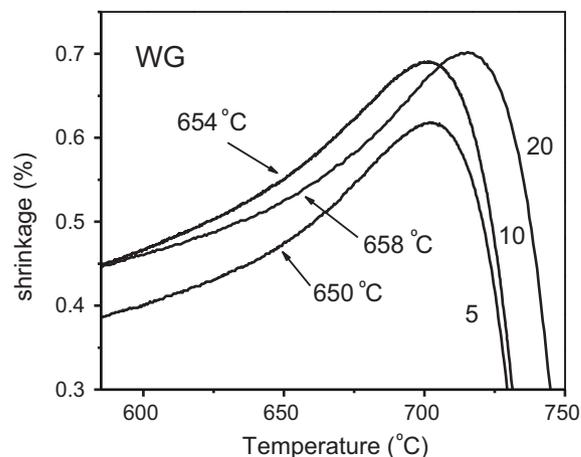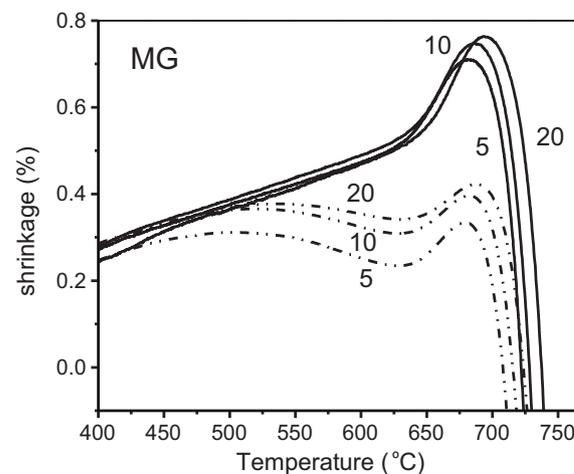
1 h at 600 °C glass powders. The results are presented in Fig. 7 with solid lines.

The densities of glass powders, before and after annealing, were measured with "AccuPyc - 1330" gas pycnometer and the result elucidate that, due to the heat-treatment the density increases from
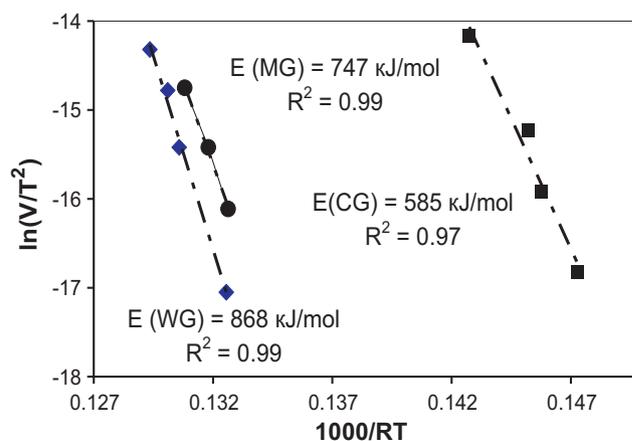

Fig. 5. Dilatometric traces in the glass transition range of CG glass powder compacts, obtained at different heating rates.

Fig. 8. Ln(v/T_x^2) versus $1/T_x$ plots and activation energies of viscous flow in the glass transition range.

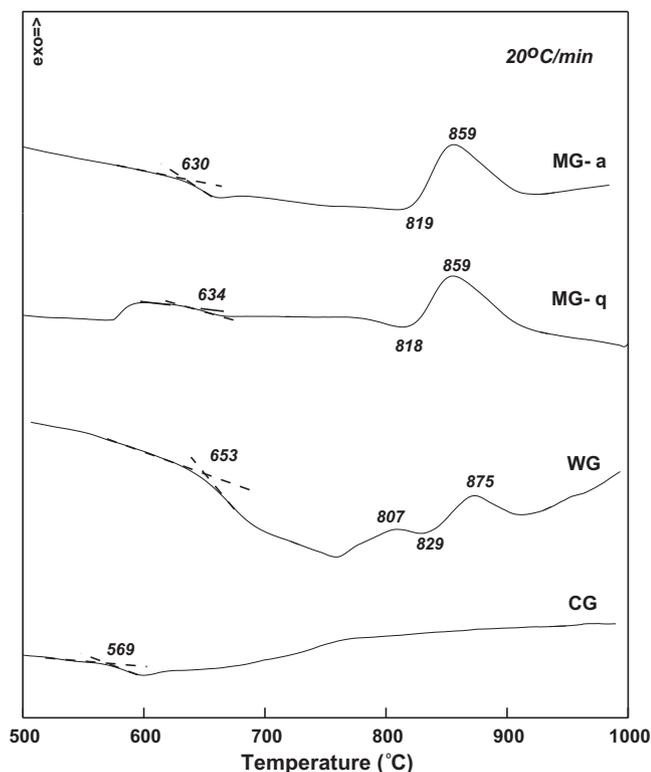**Fig. 9.** DTA results of the three glass powders, obtained at 20 °C/min.

Table 2
Absolute density, apparent density and initial porosity of the studied pressed specimens.

	Initial absolute porosity (g/cm³)	Green apparent density (g/cm³)	Initial porosity (vol%)
CG	2.496 ± 0.002	1.613 ± 0.009	35.4 ± 0.3
G	2.451 ± 0.002	1.622 ± 0.008	33.8 ± 0.3
WG	2.669 ± 0.003	1.774 ± 0.007	33.5 ± 0.3
MG	2.665 ± 0.003	1.701 ± 0.011	36.1 ± 0.4

The temperature interval between the crystallisation onset temperature and T_f, which might be used as an indication for sinterability, is ~175 °C for WG and ~190 °C for MG. Considering also, that the Fe^{2+} oxidation in WG leads to an increasing of the viscosity, might be assumed that MG glass powders can be characterised with a better sinterability.

The results for the absolute and apparent densities of the "greens'" and the corresponding initial porosities are summarised in Table 2. Assuming that no residual porosity remains in the sintered samples, no crystallization and/or deformation carries out during the thermal treatments and no anisotropy is observed (i.e. the shrinkages in the three directions are identical) these porosity values can correspond to maximum linear shrinkages of ~13.5% for CG, ~12.7% for WG and ~13.9% for MG.

Fig. 10 presents the sintering curves of CG glass powder compact at 10 C/min, obtained with contact dilatometer (traced lines) [17] and optical dilatometer (solid lines), respectively. It is well seen that the sintering, measured with contact dilatometer, is accelerated: the densification starts earlier and caries out at higher rate. In addition, when contact dilatometer is used significant shrinkage anisotropy is observed and, in many cases, the end of sintering overlaps with the beginning of deformation. Contrary, the reached linear shrinkage of ~12.5% with the optical dilatometer is in a good agreement with the expected value.

Figs. 11 and 12 summarise sintering curves with optical dilatometer at different heating rates of MG and WG, respectively. In the model glass, as well as in CG, the sintering is not seriously influenced by crystallisation process and completed before formation of distinguished amount of crystal phase. As a result, the final degrees of densification at different heating rates are similar (~12.5–13%).

Contrary, in WG composition, where the crystallisation carries out at higher viscosities, the sinter-ability depends on the heating rate. At 2 °C/min the final linear shrinkage is ~8.5%, whereas at 20 and 30 °C/min the sintering completes at linear shrinkage of
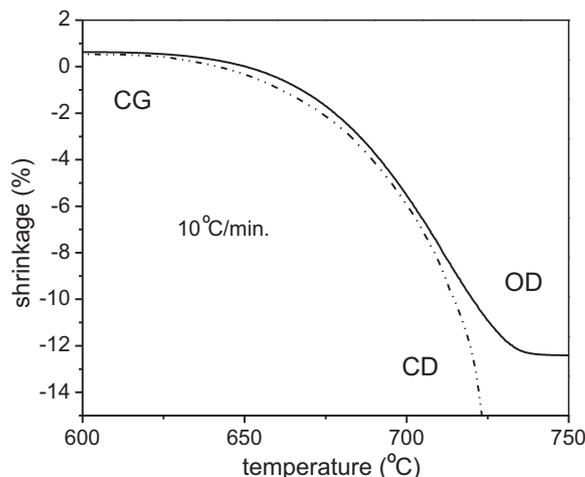
$2.665 ± 0.003$ to $2.698 ± 0.003$ g/cm³. XRD analysis shows that no crystallization carries out during the made thermal cycle, which means that the observed density rise is not related to a crystallisation process. Similar variations because of annealing are also reported for other glasses [4,22,24].

The kinetics results, obtained with the annealed MG glasses powders correspond to E_{Tg} of 747 kJ/mol (see Fig. 8). The comparison of the values of activation energy of viscous flow in glass transition range of the three studied glasses reasonable demonstrates an increase of E_{Tg} with the rise of T_f.

In addition, the results with the quenched MG powders highlight an interesting possibility for estimation of the temperature region of glass transition even for very rapidly cooled glasses. This peculiarity might be very useful in many cases (small amount of the glass samples, compositions with high crystallization ability, etc.). It can be noted that similar experiments are not possible with a bulk sample, because it obligatory can be annealed before cutting and polishing; otherwise it will crash during the mechanical treatments.

3.3. Evaluation of activation energy of sintering

DTA traces of the three glass powders, obtained at 20 °C/min, are shown in Fig. 9. CG presents only a glass-transition and the estimated T_f is in a good agreement with one of the corresponding dilatometric plot. The result with WG highlight a glass transition in the region of 650 °C, oxidation exo-effect (due to surface Fe^{2+} into Fe^{3+} transformation) [25,26] at about 800 °C and crystallisation exotherm with peak temperature at 875 °C. For MG glass are presented results with both quenched glass powders (labelled as MG-q) and annealed glass powders (labelled as MG-a). It can be noted that the observed differences in the range 550–650 °C are typical for the variations of the DTA signals between annealed and very fast quenched glasses [9]. At the same time the crystallisation exo-effects of both samples are practically identical.

Fig. 10. Sintering curves of CG glass powder compacts at 10 C/min, obtained with contact dilatometer (traced lines) [17] and optical dilatometer (solid lines).
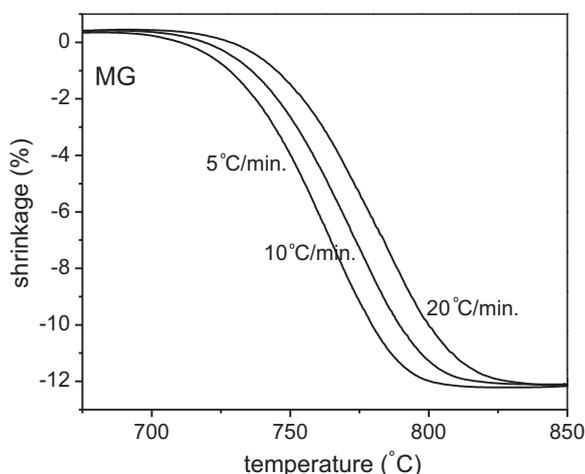
Fig. 11. Sintering curves with optical dilatometer of MG glass powder compacts, obtained at different heating rates.

Fig. 13. Variations of activation energies of sintering vs. shrinkage, obtained with optical dilatometer (WG, MG and CG) and with contact dilatometer (CG*)[17].

~10.5%. The difference of ~2% corresponds to ~6% lower porosity in the samples, heat-treated at high heating rates. Similar variation in the total porosity (~7%) was also measured by pycnometric measurements in an earlier study [27]. Other details for the sinter-crystallisation of WG glass-ceramic are published in a previous work [16].

The improvement of densification in sintered glass-ceramics with the rise of heating rate is a well known phenomenon [28–31]. However different aspects for the relationship between phase formation and densification are not yet well known. The application of "in situ" methods, as the presented optical dilatometry, might elucidate interesting details and can give reasonable kinetics results.

The variations of activation energies of sintering, E_{sin}, of the three glasses vs. shrinkage, obtained by Eq. (2), are summarised in Fig. 13. In the same figure results with CG glass powders, obtained with contact dilatometer, are shown for a comparison [17].

Due to the additional "push" rod force the measured activation energies of sintering with contact dilatometer are lower than the expected ones and remain nearly constant with the shrinkage increasing [17,31].

At the same time, E_{sin}, measured with optical dilatometer, are realistic and decrease with the shrinkage increasing. At linear shrinkage of 1% the estimated activation energies of sintering are comparable to the corresponding E_{Tg} which is a logical result; then
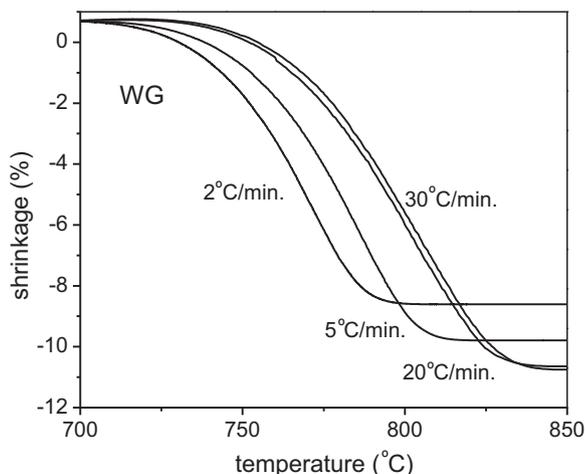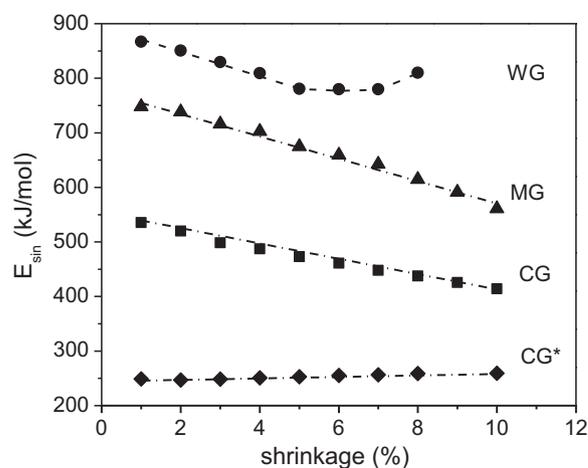
their values decrease with the temperature rise, in an agreement with the diminishing of activation energy of viscous flow. In CG and MG this decrease is observed in the whole sintering interval, while in composition WG, due to the begging of some phase formation, E_{sin} starts to increase at linear shrinkages of ~7%.

4. Conclusion

By using optical dilatometer and pressed glass powders a new method for evaluation of glass transition temperatures and fictive temperatures of quenched and annealed samples is demonstrated. In addition, applying different heating rates, the activation energy of viscous flow in the glass transition range was also estimated.

The possibility for correct measurements of the activation energy of sintering, E_{sin}, is also highlighted using glasses with different crystallisation ability. The obtained values are realistic and higher than ones, evaluated with traditional contact dilatometer. In glasses with low crystallization trend E_{sin} decreases with the temperature rise in the whole sintering range; in glasses with higher crystallization ability, E_{sin}, starts anomaly to increase with the beginning of the phase formation.

Acknowledgment

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Fig. 12. Sintering curves with optical dilatometer of WG glass powder compacts, obtained at different heating rates.

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