MEASUREMENT OF OPTICAL TRANSMITTANCE - A NOVEL METHOD FOR DETERMINATION OF THE GLASS TRANSITION TEMPERATURE OF TRANSPARENT GLASSES

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A light beam thermal analysis (LBTA) has been applied for determination of the glass transition region (T_g) of Y_2O_3-Al_2O_3-SiO_2 glasses containing between 0 and 20 mol.% of CaO. The temperature dependence of the optical transmittance of glass plates with parallel surfaces and with controlled surface roughness was determined. Healing of defects on the glass surface by viscous flow in the temperature region close to T_g was observed, resulting in increased transmission of visible light through the specimen. The T_g values measured by LBTA are in a comparatively good agreement with the results obtained by differential thermal analysis (DTA).

INTRODUCTION

The work applies the new thermoanalythical method described recently in literature - Light Beam Thermal Analysis (LBTA) [1 - 4] for determination of the glass transition region of transparent glasses. The method has been already successfully applied for determination of the temperature of crystallization of various materials. The measurement of glass transition temperature is based on the fact that in certain temperature region glass transforms to a metastable liquid. This is reflected, for example, in a different slope of the dependence of the thermal expansion coefficient below and above the transition region. Above the glass transition temperature a viscous flow of the metastable liquid can be observed. As a consequence, the surface defects (scratches) are healed. At temperatures just above T_g the process is relatively slow, due to high viscosity of the metastable liquid (the viscosity near T_g temperature is approximately 10^{13} Pas, while at the glass softening point it reaches the value close to $10^{7.65}$ Pas). The healing is comparatively faster in glasses with high surface tension. High density would also promote healing, due to increased influence of gravity on the shape change of surface asperities. However, the influence of density is expected to be negligible. The healing of surface defects increases the quality of surface finish of glass, resulting in increased transmittance of visible light. The present work attempts to utilize the effects described, for direct determination of glass transition region/temperature in transparent glasses. The results obtained are compared to those acquired in the same time-temperature schedule by commonly used method of T_g determination - differential thermal analysis (DTA).

EXPERIMENTAL

The glasses were prepared by mixing the appropriate quantities of high purity reagents Al_2O_3 (99.9 %), Y_2O_3 (PIDC, USA grade 4N-99.99 %), SiO_2 (pure, Reachim, St. Petersburg), $CaCO_3$ (p.a., Lachema, Brno) to yield 100 g of glass. The powders were dry-mixed and melted in a 10% RhPt crucible in air in an electric furnace and held for 5 h at the melting temperatures between 1570 - 1630°C. The homogeneity was ensured by repeated fritting and hand mixing in the course of melting. The melt was poured onto a copper plate. The samples were subsequently annealed in a muffle furnace for 4 h at 800 - 850°C. After annealing, the samples were cooled down to room temperature in the furnace. The glasses were prepared with constant Y_2O_3/Al_2O_3 molar ratio equivalent to the Y_2O_3/Al_2O_3 ratio in YAG crystal. The general formula of glass can be expressed as $(Y_3Al_5O_{12})_{x-z}.(SiO_2)_y.(CaO)_z$ with CaO content z ranging from 0 to 20 mol.%. The content of silicon oxide was kept at constant level, see table 1.

Table 1. Chemical composition (as-weighed) of measured glasses (mol fraction).

glass	x(CaO)	x(Y_2O_3)	x(Al_2O_3)	x(SiO_2)
YAGSiO2	0.00	0.1417	0.2361	0.6222
YASiCa01	0.05	0.1229	0.2079	0.6222
YASiCa02	0.10	0.1042	0.1736	0.6222
YASiCa03	0.15	0.0854	0.1424	0.6222
YASiCa04	0.20	0.0666	0.1111	0.6222

Rectangular plates with dimensions of approximately 10×10×2 mm and with parallel bases were prepared by cutting the pieces of glass with diamond wheel. The plates were ground with diamond wheel 160/125 μm so that specimens with controlled surface roughness were prepared. In order to evaluate the influence of surface roughness on the change of the optical transmission, surface of three specimens of the sample YASiCa01 was ground with three different diamond wheels with surface roughness 160/125, 50/40, and 22/15 μm.

The ground surfaces were examined by SEM (TESLA BS400) in order to evaluate the morphology and size of surface asperities. The parameters of surface roughness R_a and R_z have been determined by a standard device (Hommel Tester T-1000) for measurement of surface roughness. The mean arithmetic deviation along the measured profile R_a is defined by equation (1):

$$R_a = \frac{1}{l_m}\int_0^{l_m} |y| \mathrm{d}x$$

where l_m is the total measured path length, y is the vertical deviation from the ideally smooth surface, and x is a horizontal co-ordinate in an arbitrary chosen path direction. The origin of the y-axis, i.e. the level of ideally smooth surface, is given by the equation:

$$0 = \int_0^{l_m} y \mathrm{d}x$$

The R_z value is defined as the mean of five average deviations from ideally smooth surface along the measured path divided into five equal parts.

The ground glass plate has been then placed on a platinum holder with a sight hole and fixed in a high temperature tube furnace equipped with a source of monochromatic red light and heated with 10°C/min up to 1250°C. The experimental arrangement allowed for correction on the background radiation from the furnace. The intensity of the light beam passing perpendicularly the specimen has been measured by the Si-photodiode. Detailed description of the experimental arrangement is given elsewhere. [1]

In order to evaluate the influence of heating rate on the rate of healing of surface flaws three specimens of the same composition YASiCa01 were ground with 160/125 μm diamond wheel and the temperature change of the optical transmission was observed at three different heating rates 1, 10, and 20°C/min.

Table 2. The roughness parameters of the YASiCa01 glass ground by 22/15, 50/40 and 160/125 diamond wheels (l_m).

diamond wheel	R_a (μm)	R_z (μm)
22/15	0.69	5.48
50/40	1.22	9.49
160/125	1.49	10.14

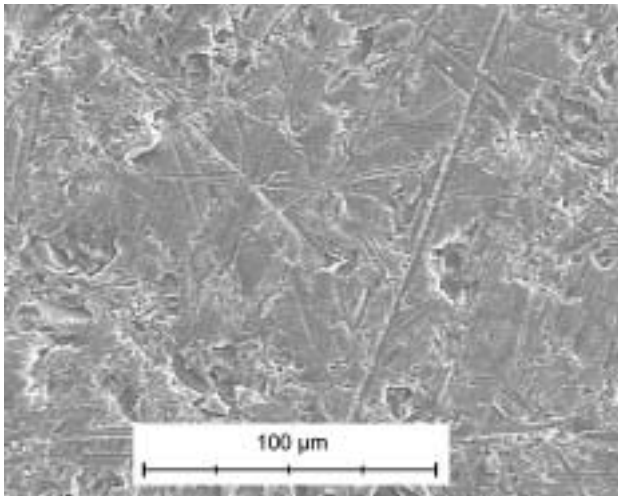
Approximately 20 mg of powdered glass was melted in platinum crucible and examined by a SDT 2960 (T.A. Instruments) DTA/TG thermoanalysis equipment in temperature range between 25 and 1200°C, heating rate 10°C/min.

RESULTS AND DISCUSSION

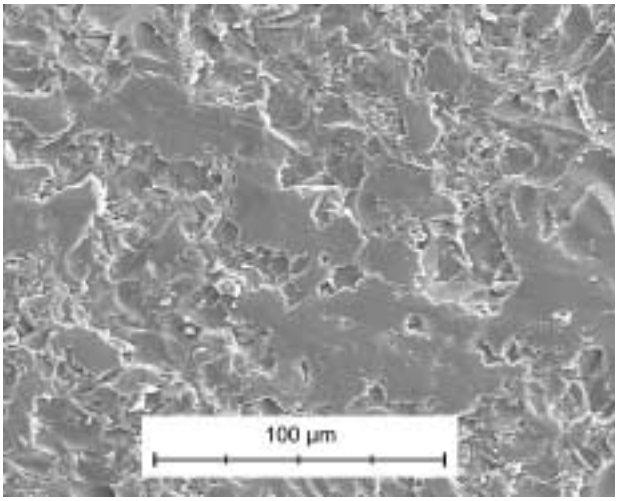
The SEM micrographs of ground surfaces are shown on figure 1. The surface roughness progressively increased with the roughness of diamond wheels. The results of determination of parameters of the surface roughness are given in table 2.

The temperature change of optical transmission (OT) of five glass specimens with different composition are shown in figure 2. At the beginning of the measurement the optical transmission of all the samples measured has approximately the same (low) value given by the surface finish of glass. At certain temperature a slow increase followed by the steep growth of the optical transmission is observed. The OT comes through the maximum, followed by the steep decrease at higher temperature so that the transmission approaches zero at the temperature of about 100°C higher than the temperature of the peak maximum. The observed changes can be attributed to changes in the sample surface finish and to the change of the overall sample geometry. The initial increase of OT is due to the healing of surface defects, followed by the maximum at the temperature when all the surface asperities disappear leaving smooth surface. The subsequent decrease at higher temperatures is caused either by crystallization of glass, or by change of the shape of the specimen from the plate with parallel bases into the lentil-shaped body. This change results in dispersion and reflection of light at the glass-air interface and reduces effectively the intensity of the transmitted light beam to values close to zero. It has to be mentioned that the final light transmission of the lentil-shaped specimens is, due to the mentioned effects, lower than the OT of the initially flat ground specimens.

The temperature of the onset of increase of the OT is considered to be the temperature of glass transition, T_g. The temperature of the onset has been determined as the temperature, where the deviation from the horizon-



a)



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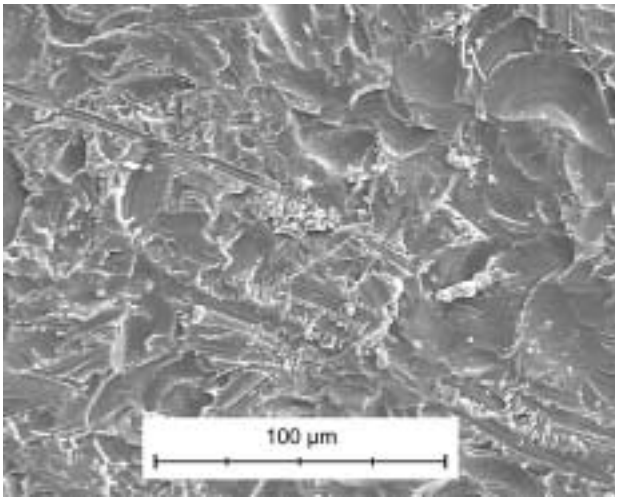

c)

Figure 1. The SEM micrographs of glass surfaces ground with a) 22/15, b) 50/40 and c) 160/125 diamond wheel

tal baseline (identical to the initial transmittance of the ground sample) could be first observed, i.e. the temperature where the first derivation of the smoothed curve achieved value > 0. As can be seen from the figure 3, this temperature is shifted to higher values with decreasing CaO content in glass, which is in agreement with the assumed structural function of calcium ions as glass network modifiers. [5]

In order to compare the results acquired from the OT measurement with the data obtained by a standard, well established method, the Tg values were measured also by DTA. The sections of the DTA curves in the relevant temperature region are shown in figure 4. The T_g values are listed in table 3. The overall trends are the same as in the case of the OT measurement (figure 3): the T_g value increase with decreasing CaO content in studied glasses. The absolute values, are however, somewhat lower than those measured by LBTA. This is perhaps not surprising if one keeps in mind, that the healing of defects is a relatively slow process influenced by relatively high viscosity of glass in the T_g region. The healing of defects is therefore at the given heating rate 10°C/min optically detected at temperatures which are higher then the real initiation temperature of the healing process. The apparent Tg value as measured by LBTA should therefore depend on the heating rate. Moreover, temperature of the onset of the OT increase can be markedly influenced by various kinetic factors, which depend on the surface energy, and therefore on the surface finish of glass specimens. The influence of all these factors has been investigated in this study.

The T_g values determined from the increase of the OT value are summarized in table 3. In the method presented in the paper the temperature of the onset of increase of the OT was considered as T_g. This is based on the assumption that the glass surface consists of surface asperities with various shapes and sizes and hence, with various surface energies. Considering the normal distribution of sizes of surface asperities, the temperature of the onset of increase of the OT corresponds to healing of "smallest" asperities with the highest values of surface energies. However, as obvious from the figure 1, grinding glass with a diamond wheel with high surface roughness yields the surface finish where not only the average, but the whole surface asperities size distribution is shifted to higher values. The specific surface energy of such specimen should be then much

Table 3. Glass transition temperatures as measured by DTA and LBTA and the difference between the two methods.

glass	T_g (°C) (DTA)	T_g (°C) (LBTA)	ΔT_g (°C)
$YAGSiO_2$	919	970	51
YASiCa01	909	948	39
YASiCa02	894	923	29
YASiCa03	878	913	35
YASiCa04	859	868	9

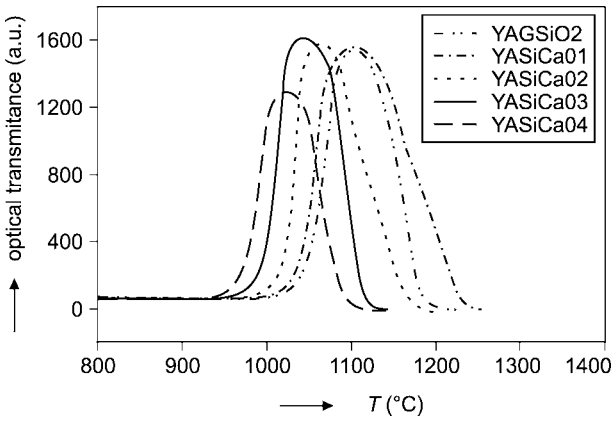

Figure 2. The optical transmission of the $YAGSiO_2$ glasses with various CaO contents as a function of temperature.

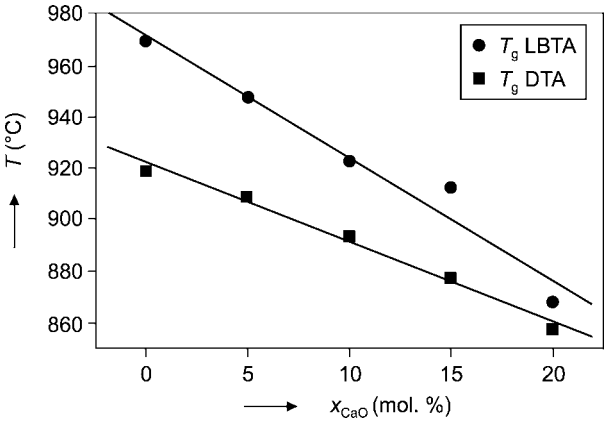

Figure 3. Comparison of the T_g values of $YAGSiO_2$ glasses with various CaO contents, as measured by DTA and LBTA methods.

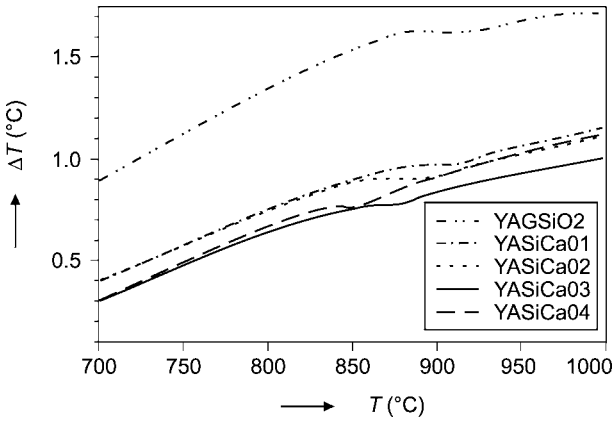

Figure 4. The relevant sections of DTA curves of $YAGSiO_2$ glasses with various CaO contents.

lower then that of the finely ground glass. Then, however, one would expect that the apparent T_g as measured by LBTA would be surface roughness dependent. Indeed such an effect has been observed when measuring the YASiCa01 glass ground with diamond wheels with various roughness, as shown in figure 1 and table 3. The dependence of the temperature of the onset of the OT on the mean deviation from ideally smooth surface R_a is shown in figure 5. The intersection of the fitted straight line with the y-axis yields a T_g value, which is considered to be representative for given glass and the respective heating rate. By such extrapolation to "zero" surface roughness the apparent T_g value is 900°C, resulting in a difference of only 9°C compared to the Tg value measured by DTA.

In real measurement, a significant dependence of the apparent glass transition temperature on the heating rate must be expected. The main reason is high viscosity of glass in the glass transition region and hence, very low healing rate of surface defects. The surface asperities with highest surface energy heal first and time is required until the healed fraction of surface defects is sufficient to result in any observable change of the optical transmittance. In the regime of finite linear increase of temperature this results in overestimation of the glass transition temperature. The deviation from real T_g value would increase with increasing heating rate during the measurement. Figure 6 illustrates the heating rate dependence of the apparent glass transition temperature of the YASiCa01 glass ground with the 160/125 diamond wheel and heated with 2, 5, 10 and 20°C/min. An approximately linear decrease of the apparent glass transition temperature with decreasing heating rate could be observed, with difference of 40°C between the glass transition temperature measured at heating rates of 2 and 20°C/min.

The results obtained justify the use of temperature dependence measurement of the optical transmittance of transparent or translucent glasses, as a new method for determination of T_g. The accuracy of the method is in reasonable limits as the other established methods often yield results that for the same glass differ by several tens of degrees. [6] The verification of the method for broader range of industrial glasses along with computer modeling of processes resulting in healing of surface defects and increase of light transmittance is presently under progress. Further experimental work is required in order to evaluate relations between the surface roughness, heating rate and the measured glass transition temperature.

CONCLUSIONS

A new method (LBTA) that can be successfully applied for measurement of T_g of transparent glasses is based on the change of optical transmission of glass plates due to healing of surface asperities above T_g by

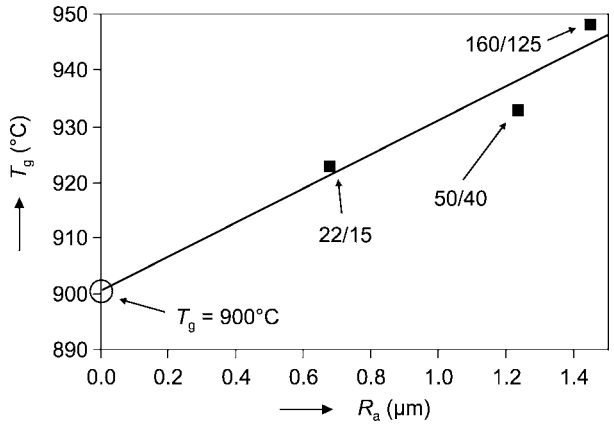

Figure 5. Surface finish dependence of the apparent glass transition temperature of the YASiCa01 glass.

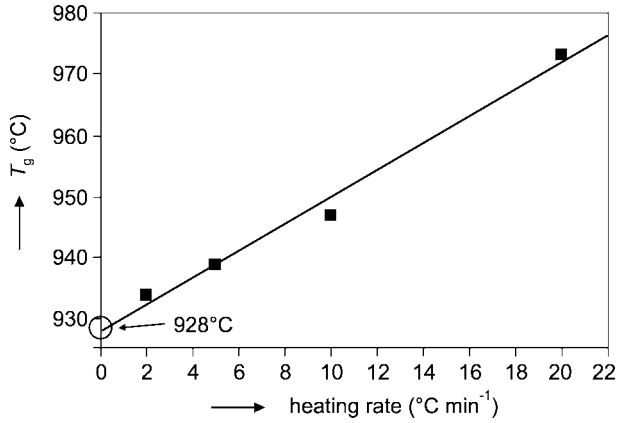

Figure 6. The heating rate dependence of the measured apparent glass transition temperature of the YASiCa01 glass.

viscous flow. The method yields the T_g values, which are in a relatively good accord with those obtained by DTA measurement. The accuracy of the measured T_g values can be improved by extrapolation of the data measured at various surface finishes to "zero" surface roughness. Further investigation, especially focused on improving the accuracy and reproducibility of the method, accompanied by the computer modeling of processes responsible for the change of the optical transmittance are recently in progress. The comparison with the results of thermo-dilatometry measurements is needed to appreciate the accuracy and correctness of the proposed method in a more general way.

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MERANIE OPTICKEJ PRIEPUSTNOSTI - NOVÁ METÓDA STANOVENIA TEPLOTY SKLENÉHO PRECHODU TRANSPARENTNÝCH SKIEL

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V prezentovanej práci sa skúmala teplotná závislosť zmeny optickej priepustnosti (OP) skiel v systéme Y_2O_3-Al_2O_3-SiO_2 s obsahom od 0 do 20 mol.% CaO. Na meranie OP sa použili platničky s hrúbkou 2 mm, s paralelnými stenami a s definovanou drsnosťou povrchu, ktorá sa dosiahla brúsením diamantovým kotúčom. Pri meraní OP sa zistilo, že po počiatočnej, relatívne nízkej priepustnosti spôsobenej rozptylom svetla na zdrsnenom povrchu, dochádza k náhlemu zvýšeniu OP v oblasti Tg skla, ktorá po dosiahnutí maxima pri teplote o približne 100°C vyššej ako T_g opäť klesá až na prakticky nulovú hodnotu. K nárastu OP v oblasti T_g dochádza v dôsledku vyhojovania povrchových vád skla viskóznym tokom. Následný pokles je spôsobený buď zakalením skla v dôsledku tvorby a rastu kryštalizačných zárodkov, alebo zaobľovaním hrán meranej vzorky, ktoré vedie až k vytvoreniu šošovkovitého telieska, kde potom dochádza k prakticky úplnému odrazu a rozptylu svetelného lúča na rozhraní sklo - vzduch.

Efekt vyhojovania defektov na povrchu platničiek sa v práci využil na stanovenie T_g skúmaných skiel. Za teplotu T_g sa považuje teplota, pri ktorej na krivke závislosti OP od teploty začína rásť optická priepustnosť, a ktorá sa považuje za teplotu pri ktorej dochádza k vyhojovaniu defektov s najvyššou povrchovou energiou. Vyhodnotila sa tiež závislosť nameranej hodnoty T_g od experimentálnych parametrov, menovite od drsnosti povrchu vzorky a od rýchlosti ohrevu. Teploty T_g stanovené pomocou diferenciálnej termickej analýzy sa použili na verifikáciu výsledkov získaných meraním OP. Obe metóde poskytli hodnoty líšiace sa pre jednotlivé sklá o 9 až 50°C, čo možno považovať za veľmi dobrú zhodu. Obe metódy potvrdili rovnaký trend poklesu T_g so stúpajúcim obsahom CaO v meraných sklách, čo je v dobrej zhode s predpokladanou štruktúrnou funkciou CaO ako modifikátora.