



Variations in non-isothermal surface crystallization kinetics due to minor composition changes



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ABSTRACT

The aim of present article is to analyze experimental results on the non-isothermal kinetics of crystallization in dependence of minor composition changes. We investigate the role of network formers (Al_2O_3) and network modifiers (Na_2O), respectively, on the kinetics of overall crystallization of three glasses, forming about 60% diopside ($\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$) by surface crystallization. The shift of crystallization to higher temperatures follows the viscosity rise due to the composition changes and the phase formation always carries out at similar viscosities. In addition, the variations of activation energy of crystallization, E_a , on the composition is relatively weak, although the temperature interval at which the process appears depends on it. The results also highlight that the degree of transformation, corresponding to the exo-peak temperature, T_p , depends on the glass composition and slowly decreases with the increasing of heating rate.

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1. Introduction

The kinetics of transformation of glasses into glass-ceramics has been thoroughly investigated under isothermal as well as under non-isothermal conditions in terms of the KJMA equation, derived independently by Kolmogorov [1], Johnson & Mehl [2] and Avrami [3,4]. This equation sets a time, t , dependence of the transformation rate, x , as follows:

$$x = 1 - \exp\left(-\left(\frac{t}{\tau}\right)^m\right) \quad (1)$$

Here τ is the characteristic crystallization time. The power m accounts for the mechanism of crystal growth (mono-, bi- or three-dimensional) as well as for the factors controlling the crystallization process (nucleation or growth from active centers; linear growth or diffusion controlled one).

When crystallization occurs in confined spaces, such as powders, the overall kinetics and in particular the parameter m depend on the grain size [5]. When grains are relatively large, a growth of needle-like crystals perpendicular to the grain surface is frequently observed. On the other hand, in fine powders the crystals remain more or less isometric until the end crystallization process. This is a strong indication that when crystallization occurs in medium-sized grains the power m changes during the process, because the process often begins from several active centers on the surface of the particles. Therefore crystallization starts as three dimensional, $m = 3$. Later on, crystalline shell is

formed on the surface and the process continues inwards as quasi one-dimensional [6,7].

The temperature (respectively the rate of temperature change) as well as the grain size and the composition of the ambient phase (correspondingly the change in melt composition during phase separation) are among the most important parameters controlling the overall kinetics of phase transition. Upon crystallization, the residual matrix is enriched either in network former or in network modifier. The aim of the present article is to analyze experimental data in order to find reliable modes of interpretation of experimental results on kinetics of crystallization in dependence of composition changes.

2. Experimental

The milling of obtained glass frits was carried out in agate mill at 300 turns per minute using portions of 50–60 g frit and milling time of 20 min. In the present work powder samples with fraction size between 75 and 125 μm were used. Non-isothermal DTA analysis were performed (Linseiz L81) applying 4 different heating rates, q : 5, 7.5, 10 and 20 $^\circ\text{C}/\text{min}$.

The investigated glasses belong to the well-studied diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$)–albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) system [8,9], which phase diagram shows a large and a narrow crystallization fields for diopside and albite, respectively, resulting in the formation of diopside as single crystal phase. In addition, due to the big density difference between the crystal and amorphous structure without nucleation agents the diopside is formed only by surface crystallization. It is also important that in DTA experiment similar fractions of these glasses show the crystallization peaks at about 200 K below the liquidus

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(i.e. the experiments carried out at similar and sufficiently high supersaturation).

In [9] it was also shown that the studied three compositions form similar amount of crystal phase (about 60 wt.% diopside) by surface crystallization, as well as similar percentages of crystallization induced porosity (about 9 vol.%). This kind of porosity is a consequence of the significant density difference between the parent glass and the newly formed crystal phase, which is typical for the diopside glass-ceramics [9,10]. The crystallization induced pores are formed in the centers of the particles, which lead to a decreasing of the crystal length and to an increasing of the Avrami parameter [6].

Fig. 1 shows the DTA results at used heating rates for the three compositions. The shift of crystallization peaks, T_p , to higher temperatures with the rise of viscosity is clearly seen. It is evident that the area of the peaks at equal heating rates is comparable, which confirm the similar amount of formed crystal phase. Note that the intensity of the DTA signal is proportional to the heating rate. At the same time, some differences in the shapes of the exo-effects and their symmetry are observed.

3. Results

Glass batches were prepared by mixing SiO_2 (>99.5%) with technical $\text{Al}(\text{OH})_3$, CaCO_3 , MgCO_3 and Na_2CO_3 . The theoretical glass compositions (labeled *Di*, *DiNa* and *DiAl*) are reported in Table 1, together with the values, obtained by XRF, X-ray fluorescence, analysis (Spectro XEPOS) after melting. The melting of glasses was carried out in 500 ml corundum crucibles for 2 h. *Di* was melted at 1500 °C, while *DiNa* and *DiAl* at 1450 and 1550 °C, respectively. The melts were fritted and the obtained frits were smashed, milled and sieved. Due to the high amount of CaO and MgO in the parent compositions, it can be assumed that Al_2O_3 plays as glass former substituting SiO_2 in the glass network, while Na_2O is a typical glass modifier.

The viscosity variations of these compositions were estimated by the following equation:

$$\log \eta = \log \eta_0 + (13 - \log \eta_0) \left(\frac{T_g}{T} \right)^\alpha \quad (2)$$

Table 1

Chemical compositions, in mol%, of studied glass compositions. All columns t give composition according to syntheses while that in columns entitled a are compositions according to analyses.

	Di		DiAl		DiNa	
	t	a	t	a	t	a
SiO_2	54	53.0 ± 0.1	54	53.5 ± 0.1	54	53.2 ± 0.1
Al_2O_3	2	2.1 ± 0.2	4	5.2 ± 0.2	–	0.7 ± 0.2
CaO	21	22.1 ± 0.1	21	19.6 ± 0.1	21	22.6 ± 0.1
MgO	21	20.6 ± 0.2	21	17.9 ± 0.2	21	19.6 ± 0.2
Na_2O	2	2.2 ± 0.2	–	–	4	3.9 ± 0.2

Here η_0 is a pre-exponential constant, α is dimensionless “fragility” parameter, which accounts how fast viscosity changes with temperature [12,13] and T_g is the temperature (in [K]) at which the equilibrium viscosity is equal to 10^{13} [dPa.s]. The values of parameters $\log \eta_0$, α and T_g are determined according to recommendations given in [13] and the program, free for download from [14]. The corresponding values in dependence of compositions are listed in Table 2. It is seen that while the T_g depends on the quantity of network formers or network modifiers the other two parameters, fragility α and limiting high temperature viscosity $\log \eta_0$ remain unchanged in these composition limits. Traditionally, the glass transition temperatures T_g are experimentally determined as the onset points at which, in dependence of the rate of the up scan, the non-equilibrium glass starts to relax with observable rate. This “experimentally” obtained glass transition temperature depends on heating rate, while the “thermodynamic” T_g is unique equilibrium property of the system. These two definitions are suitable because, on average, T_g does not deviate from the “kinetic” T_g by more than 1%. (See Tables 3 and 4)

4. Discussion

In order to estimate the changes in symmetry of crystallization peaks the experimental DTA data was integrated and the degree of transformation, x_p corresponding to the peak temperature, T_p , was evaluated for each DTA run. The results for obtained x_p in dependence on the

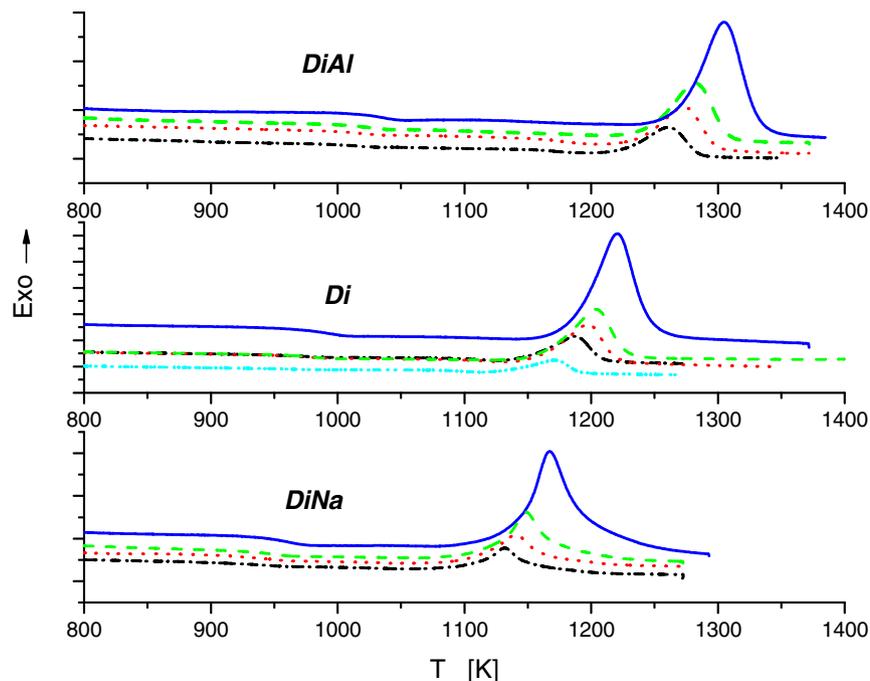


Fig. 1. The raw DTA data from the 3 compositions. The heating rates are: — solid line $q = 20$ [K/min]; - - - Dashed line $q = 10$ [K/min]; ... Dotted line $q = 7.5$ [K/min]; - · - Dash Dot line $q = 5$ [K/min]; - · · - Dash Dot Dot line $q = 2.5$ [K/min].

Table 2

The Values of parameters controlling viscosity Eq. (2). Parameter α is dimensionless fragility, the parameter $\log \eta_0$ is in [dPa.s], T_g is the theoretical temperature [K] at which $\log \eta = 13$ [dPa.s].

Composition	$\log \eta_0$ [dPa.s]	T_g [K]	α
Di	0.3	991	4
DiAl	0.3	1036	4
DiNa	0.3	949	4

heating rate q are shown in Fig. 2. It is seen that, on average, for the Di composition $x_p \approx 0.62 \pm 0.03$, for DiAl $x_p \approx 0.59 \pm 0.02$ while for DiNa composition the position of the peak is essentially lower, $x_p \approx 0.47 \pm 0.03$. Also, a trend for a decreasing of x_p with the increasing of the heating rate is clearly observed.

We firstly determine the activation energy for crystallization from the DTA curves using the Kissinger's equation [15,16] relating the temperature T_p of the crystallization peak and the heating rate q in the following form

$$\ln\left(\frac{q}{T_p^2}\right) = -\frac{E}{RT_p} + \text{const.} \quad (3)$$

The derivation of Eq. (3) is based on analyses of the KJMA equation [17] under assumption that the degree of transformation at the temperature T_p of the DTA peak always is $x_p = 0.63$. However, Fig. 2 demonstrates that the degree of transformation, corresponding to the peak temperature varies with the glass composition and the heating rate.

Recently [18] we demonstrated that expression, similar to Eq. (3) is not limited by the assumption of validity of the KJMA equation, (Eq. (1)). Moreover, it becomes universal if, instead of T_p , we use any temperature, T_x , at which a given value of x is reached.

$$\ln\left(\frac{q}{T_x^2}\right) = -\frac{E}{RT_x} + \text{const} \quad (3a)$$

This important development is due to the earlier studies of Sestak et al. [19]. A similar equation was also derived by Chen [20].

The experimental results on crystallization kinetics of one of the compositions, the base glass, Di, are shown in Fig. 3 in coordinates corresponding to Eq. (3a). The open points are for $x = 0.8$, while the solid points are for $x = 0.2$. In both cases the activation energy is about $E = 440 \pm 1\%$ [kJ/mol]. As at $x = 0.8$ the temperature is higher the activation energy is slightly lower. Although the observed decrease of about 1% is within the limits of the experimental accuracy it should be noted that it has a systematic trend, in the sense that similar change appears for all compositions (not shown in the figure because they are very similar). The activation energies at several x values in dependence on composition are summarized in Table 3, together with the values obtained by Eq. (3).

While Fig. 3 illustrates data of one composition at different x value, Fig. 4 gives the data for transformation degree, $x = 0.2$, but for the three compositions. The open points \square are for the base glass, Di; the solid circles \bullet are for DiAl composition while the solid triangles \blacktriangle are

Table 4

The values of parameter m .

	Augus & Bennett	Ozawa
	m	m
DiNa	1.9	1.6
Di	2.0	1.8
DiAl	2.2	2.3

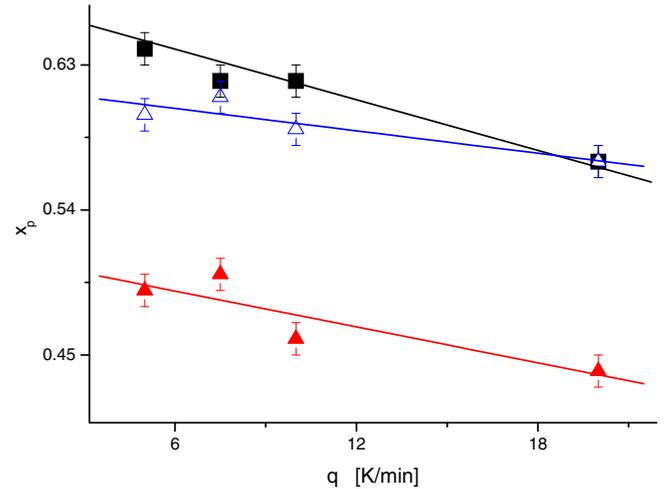


Fig. 2. The experimental data on the degree of transformation, x_p , at the maximum of the curves presented in this figure in dependence on heating rate q . The open triangles Δ are for - DiAl glass, the solid squares \blacksquare are for base composition Di while the solid triangles \blacktriangle are for DiNa composition.

for DiNa. No significant differences in the apparent activation energies are noticed.

Since for every heating rate, q , we know the temperatures T_x we can determine the corresponding viscosity using Eq. (2). For the temperatures at which $x = 0.2$ this is demonstrated in Fig. 5 in coordinates $\log \eta$ against $\log q$. Similar results are also obtained at other values of x , which elucidate that the phase formation in the three glasses carries out at very similar viscosities; the differences between estimated viscosities at each degree of transformations are less than one order. Intuitively one expects that viscosity at which a given event starts is inverse proportional to the heating rate. Empirically we find a linear relationship $\log \eta = C - p \log q$ between viscosity at T_x and heating rate. The value of the constant is $C = 7.4$ for DiNa composition, $C = 7$ for the base system Di and $C = 6.7$ for DiAl. Unexpectedly, the power p is larger than one, we find that $p = 1.3 \pm 0.1$. One possible explanation could be that mobility determined from diffusion coefficient D and that determined from viscosity decouple. In fact, earlier [21,22], it was found experimentally that the Stokes-Einstein ratio, $D\eta/T = \text{const}$, is not always correct. Later on, this was also reported in Ref. [23,24]. As claimed in [22–24] the Stokes-Einstein equation does not describe the diffusion process in the case of crystallization in fragile glass-forming melts. This could be the reason for one of the possible explanations

Table 3

Activation energies determined according to Eqs. (3) and (3a).

Transformat. degree	DiAl	Di	DiNa
$x = 0.1$	$E = 420 \pm 25$ [kJ/mol]	$E = 455 \pm 20$ [kJ/mol]	$E = 365 \pm 5$ [kJ/mol]
$x = 0.2$	$E = 410 \pm 20$ [kJ/mol]	$E = 440 \pm 10$ [kJ/mol]	$E = 365 \pm 20$ [kJ/mol]
$x = 0.6$	$E = 395 \pm 10$ [kJ/mol]	$E = 450 \pm 10$ [kJ/mol]	$E = 365 \pm 5$ [kJ/mol]
$x = 0.8$	$E = 395 \pm 10$ [kJ/mol]	$E = 435 \pm 10$ [kJ/mol]	$E = 360 \pm 20$ [kJ/mol]
x_p	$E = 400 \pm 5$ [kJ/mol]	$E = 473 \pm 10$ [kJ/mol]	$E = 407 \pm 20$ [kJ/mol]

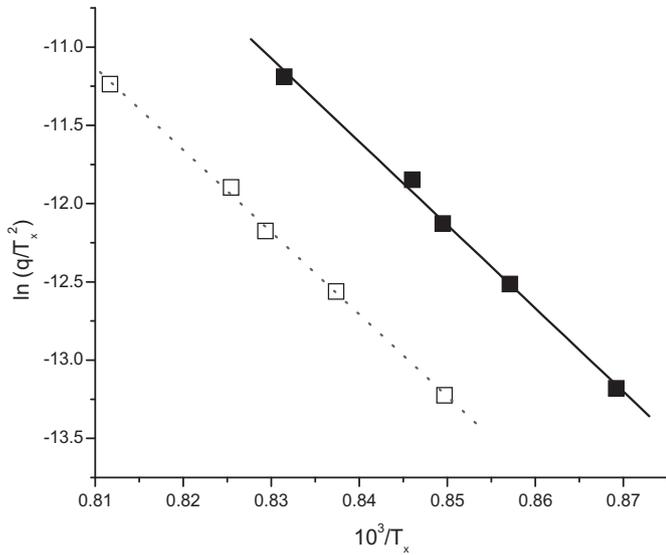


Fig. 3. The kinetics data of the base glass, Di, in coordinates corresponding to Eq. (3a). Open points and dotted line are for $x = 0.8$, the solid points and solid line are for $x = 0.2$. The activation energy E is determined from the corresponding slope.

that $p > 1$ because it give a background to assume that there could be a fractal relationship between viscosity and diffusion coefficient D .

Additional information is retrieved from the dependence of the experimentally determined glass transition temperature T_g on the heating rate, q . We test whether the viscosity values of the corresponding temperatures T_g depend on composition. At each T_g value the corresponding viscosity was determined according to Eq. (2) with parameters listed in Table 1. According to results shown in Fig. 6 the viscosity η_g at T_g depends on heating rate but is independent on composition. There is a linear relationship between $\log \eta_g$ at the experimental glass transition temperature and the heating rate, $\log q$, according to expression $\log \eta_g = 14 - \log q$, so that to the ‘thermodynamic’ definition $\log(T_g) = 13$ [dPa.s] corresponds to $q \approx 10$ [K/min]. The expected viscosity values at the glass transition temperature are in good agreement with the ones determined according to Eq. (2) giving additional prove of it validity.

The Avrami parameter m was estimated with widespread Ozawa equation [25]:

$$\left. \frac{d[\ln(-\ln(1-\alpha(T)))]}{d(\ln q)} \right|_T = -m \quad (4)$$

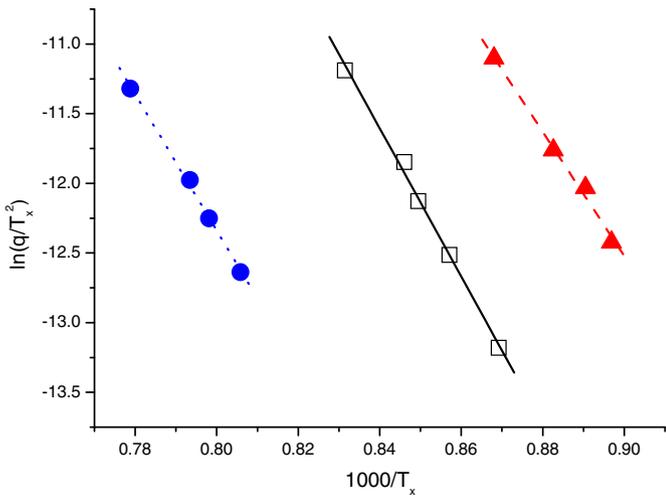


Fig. 4. Crystallization kinetics data for transformation $x = 0.2$ in coordinates corresponding to Eq. (3a). The open rectangles \square are for - base glass, Di; the solid circles \bullet are for DiAl composition while the solid triangles \blacktriangle are for DiNa composition.

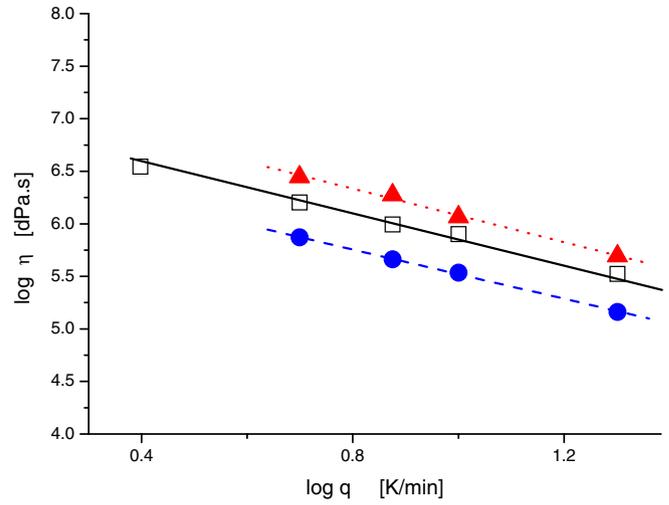


Fig. 5. The viscosity η (at which $\alpha = 0.2$ transformation is obtained) against the heating rate q in log-log coordinated. The open rectangles \square are for composition Di; the solid circles \bullet are for DiAl and the solid triangles \blacktriangle are for DiNa composition.

from exothermal peaks obtained at different q . Here the degree of transformation $\alpha(T)$ is determined, at a fixed temperature T . α value is calculated as the ratio of partial area of the crystallization peak till the temperature T .

Alternatively, m was also calculated by the Augis-Bennett equation [26]:

$$m = \frac{(2.5/\Delta w)}{(E_c/RT_p^2)} \quad (5)$$

where Δw is the width of the crystallization exotherm at half peak height.

The results, according to Ozawa and to Augus & Bennett methods are summarized in Table 2 and confirm that the Avrami parameter at surface crystallization is not always equal to one [5–7]. It is also highlighted that, notwithstanding of the similar fraction size, a trend for an increasing of the average m value with the viscosity is observed.

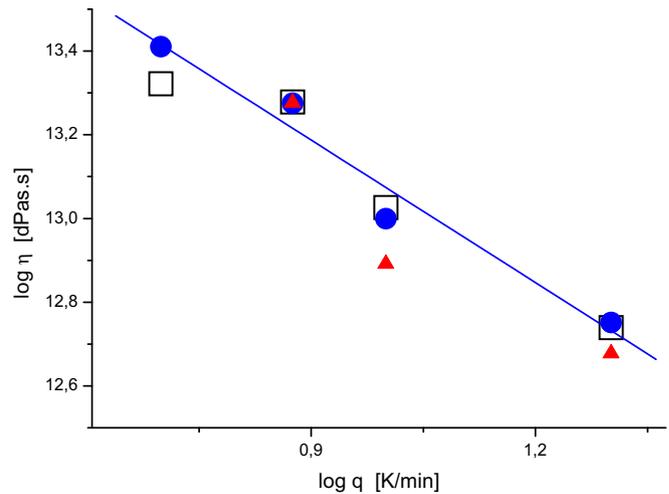


Fig. 6. Viscosity at the experimentally determined glass transition temperature in dependence of the heating rate. The open rectangles \square are for composition Di; the solid circles \bullet are for DiAl and the solid triangles \blacktriangle are for DiNa composition.

5. Conclusions

By means of analyzing experimental data we seek reliable modes of interpretation of experimental results on kinetics of crystallization in dependence of minor composition changes:

- The degree of crystallization x_p reached at the temperature T_p of the maximum of the corresponding DTA peak decreases when the heating rate increases. Therefore, the activation energy determined by the Kissinger method exceeds the one determined according to Chen [16] and Avramov & Sestak [15] method. The stronger is the dependence of the degree of crystallization x_p on heating rate the stronger deviates the activation energy determined according to the Kissinger method.
- The shift of crystallization to higher temperatures follows the viscosity rise and the phase formation always carries out at similar viscosities. As a result, the variations of activation energy of crystallization, E_a , on the composition is relatively weak, although the temperature interval at which the process appears depends on it.
- Unexpectedly, we observe a stronger than power $p = 1$ dependence of the viscosity ($\log(\eta)$) on the heating rate ($\log(q)$).
- Although the Avrami parameter m varies with chemical composition it always reminds larger than 1, the expected value for surface crystallization. Notwithstanding of the similar fraction size, a trend for an increasing of the average m value with the viscosity is observed.

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