

# Properties and structure of glasses in the system $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot 70(\text{SiO}_2, \text{GeO}_2, \text{B}_2\text{O}_3)$

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Density, refractive index, glass transition temperature and expansion coefficient of glasses in the system  $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot (70-x-y)\text{SiO}_2\cdot x\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  (mol %) have been determined. The structure of these glasses is discussed with emphasis on the shifts occurring in the boron and germanium coordination as a function of the relative concentrations of the three network-forming oxides. In  $\text{GeO}_2$ -rich glasses part of germanium is present as  $\text{GeO}_6$  octahedra, which, upon the introduction of  $\text{B}_2\text{O}_3$ , are completely transformed into  $\text{GeO}_4$  tetrahedra at  $y > 10$ .

## 1. Introduction

Interest in glasses with a relatively high BaO content arises from their potential use in optical fibre technology. Their large BaO content (combined with  $\text{GeO}_2$ ) gives these glasses a relatively high refractive index, while the increase in intrinsic scattering and absorption is relatively small [1]. Consequently these glasses are particularly well suited as core glass in low-loss fibres of high-numerical aperture, in combination with a compatible cladding glass with a low refractive index. Such fibres give a high light-incoupling efficiency, which is important in optical fibre communication systems if light-emitting diodes are used as the light source. In this paper the properties (refractive index, density, expansion coefficient and glass transition temperature,  $T_g$ ) and structure of glasses in the system  $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot 70(\text{SiO}_2, \text{GeO}_2, \text{B}_2\text{O}_3)$  (mol %) are reported.

A large number of papers have been published dealing with properties and structure of glasses that have a composition comparable with parts of the system studied here; see for example [2-10]. In oxidic glasses both boron and germanium occur as network-forming ions in two coordination sites. The coordination found in a particular glass depends to a great extent on the overall glass composition. Yun and Bray [10] using NMR (nuclear magnetic resonance) and Konijnendijk [11] using IR (infrared) and Raman spectroscopy have shown that boron in alkali (alkaline-earth) borosilicates can occur in  $\text{BO}_3$  triangles and  $\text{BO}_4$  tetrahedra.

Germanium in alkali germanosilicate glasses occurs in  $\text{GeO}_4$  tetrahedra and in  $\text{GeO}_6$  octahedra. This has been observed in studies using laser Raman spectroscopy [12], molar refraction data [6], X-ray photoelectron spectroscopy [13] and viscosity data [7].

The structure of alkali (alkaline earth) borogermanate and borogermanosilicate has been discussed on the basis of data of physical properties, such as viscosity, density and molar refraction [8, 9, 14]. It has been shown that introduction of  $\text{B}_2\text{O}_3$  in these glasses leads to a transformation of  $\text{GeO}_6$  octahedra into  $\text{GeO}_4$  tetrahedra. Maxima or minima in the relations between various physical properties and the composition of glasses which, among other components, contain  $\text{B}_2\text{O}_3$ ,  $\text{GeO}_2$  or both, were often observed in these studies. These were usually ascribed to changes occurring in the relative concentrations of the two coordination types of either boron or germanium, or both.

## 2. Experimental details

### 2.1. Melting procedures

The glasses were prepared from  $\text{K}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{B}_2\text{O}_3$  (reagent grade, E. Merck, Darmstadt, W. Germany),  $\text{SiO}_2$  ( $\alpha$ -quartz, Hereaus, Hanau, W. Germany) and  $\text{GeO}_2$  (extra pure, Hoboken, Belgium) in batches of 400 g. The target compositions of the glasses are given in Tables I to IV. The glasses were prepared by manually mixing the appropriate compounds, followed by melting in Pt-10% Rh crucibles in an electrically heated furnace. Melting

TABLE I Composition, melting temperature, refractive index, density, glass transition temperature and expansion coefficient of  $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot (70-x)\text{SiO}_2\cdot x\text{GeO}_2$  glasses (mol%)

$x$	$T_{\text{melt}}$ ( $^{\circ}\text{C}$ )	$n_{\text{D}}$	$D(\text{g cm}^{-3})$	$T_{\text{g}}$ ( $^{\circ}\text{C}$ )	$\alpha \times 10^{-7}$
0	1450	1.5612	3.108	585	104
10	1400	1.5776	3.304	—	—
20	1450	1.5944	3.456	555	107
30	1350	1.6130	3.619	—	101
40	1400	1.6319	3.780	—	105
50	1400	1.6536	3.952	525	106
60	1350	1.6737	4.123	—	—
70	1200	1.6940	4.290	505	108

temperatures  $T_{\text{Melt}}$ , which are given in Tables I to IV, varied from 1000 to  $1450^{\circ}\text{C}$  depending on the glass composition. Dried oxygen was bubbled through the melt for 1 h to achieve homogenization. After bubbling, the melt was cooled  $100^{\circ}\text{C}$  below the melting temperature in order to make it bubble-free. The melt was then poured into graphite moulds and kept at  $600^{\circ}\text{C}$  for 30 min. Subsequently the glass was cooled to room temperature by turning off the heating system of the furnace. This yielded glasses which in the region of  $T_{\text{g}}$  were cooled with  $3^{\circ}\text{C min}^{-1}$ .

## 2.2. Refractive index measurements

The refractive index  $n_{\text{D}}$  ( $\lambda = 589.3 \text{ nm}$ ) was measured with an Abbe refractometer (Zeiss, Oberkochen, Germany) with a precision of  $2 \times 10^{-4}$ . The refractive indices are given in Table I to IV and a contour map is shown in Fig. 1.

## 2.3. Density measurements

The density  $D$  was determined by weighing the glass samples both in water and in air (precision

TABLE II Composition, melting temperature, refractive index, density, glass transition temperature and expansion coefficient of  $10\text{K}_2\text{O}\cdot 20\text{BaO}(70-y)\text{SiO}_2\cdot y\text{B}_2\text{O}_3$  glasses (Mol%)

$y$	$T_{\text{melt}}$ ( $^{\circ}\text{C}$ )	$n_{\text{D}}$	$D(\text{g cm}^{-3})$	$T_{\text{g}}$ ( $^{\circ}\text{C}$ )	$\alpha \times 10^{-7}$
0	1450	1.5612	3.108	585	104
10	1350	1.5757	3.211	—	92
20	1350	1.5831	3.239	580	89
30	1200	1.5829	3.208	—	92
40	1100	1.5806	3.153	—	86
50	1100	1.5764	3.091	535	91
60	1100	1.5714	3.025	—	93
70	1000	1.5637	2.938	510	95

TABLE III Composition, melting temperature, refractive index, density, glass transition temperature and expansion coefficient of  $10\text{K}_2\text{O}\cdot \text{BaO}(70-y)\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  glasses (mol%)

$y$	$T_{\text{melt}}$ ( $^{\circ}\text{C}$ )	$n_{\text{D}}$	$D(\text{g cm}^{-3})$	$T_{\text{g}}$ ( $^{\circ}\text{C}$ )	$\alpha \times 10^{-7}$
0	1200	1.6940	4.290	505	108
10	1150	1.6782	4.148	—	103
20	1150	1.6608	3.967	520	100
40	1100	1.6241	3.591	—	93
50	1100	1.6047	3.387	515	93
70	1000	1.5637	2.938	510	95

$5 \times 10^{-3} \text{ g cm}^{-3}$ ). The densities are given in Tables I to IV and a contour map is shown in Fig. 2.

## 2.4. Expansion coefficient measurements

The expansion coefficient  $\alpha$  was determined with a horizontally placed displacement-measuring quartz dilatometer as described by Konijnendijk [11]. The expansion coefficients from  $45$  to  $400^{\circ}\text{C}$  are given in Table I to IV.

## 2.5. Glass transition temperature

The glass transition temperature  $T_{\text{g}}$  was measured by determining the temperature at which the characteristic endothermic peak in the DTA curve starts to appear [15]. DTA (differential thermal analysis) was performed by heating a crushed glass sample at the standard rate of  $10^{\circ}\text{C min}^{-1}$ . The transition temperature measured in this way is usually considered to be the temperature at which  $\eta = 10^{13} \text{ dPa sec}$  [15]. Values of  $T_{\text{g}}$  are given in Table I to IV and a contour map is shown in Fig. 3.

## 3. Discussion

The data presented in Tables II to IV and Figs. 1 to 3 show that when  $\text{B}_2\text{O}_3$  is substituted for  $\text{SiO}_2$  extremes are observed in properties such as expansion coefficient, density and refractive index. These extremes are most pronounced at  $x = 0$  ( $\text{GeO}_2$ -free glasses). Similar anomalies in physical properties when  $\text{B}_2\text{O}_3$  is substituted for  $\text{SiO}_2$  have been observed in many comparable glass systems (e.g. [2, 11]). This phenomenon is usually explained by assuming that at small contents of  $\text{B}_2\text{O}_3$ , boron is incorporated as  $\text{BO}_4$  tetrahedra in which it is surrounded by four bridging oxygens ( $\text{BO}'\text{s}$ ) resulting in a contraction of the glass network. It also explains why at  $x = 0$  no decrease of  $T_{\text{g}}$  is observed at small  $\text{B}_2\text{O}_3$  contents (Fig. 3).

Larger quantities of  $\text{B}_2\text{O}_3$  are taken up in a

TABLE IV Composition, melting temperature, refractive index, density, glass transition temperature and expansion coefficient of  $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot (70-x-y)\text{SiO}_2\cdot x\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  glasses (mol %)

$x$	$y$	$T_{\text{melt}} (^{\circ}\text{C})$	$n_{\text{D}}$	$D$ ( $\text{g cm}^{-3}$ )	$T_{\text{g}} (^{\circ}\text{C})$	$\alpha \times 10^{-7}$
5	5	1350	1.5779	3.286	—	—
10	10	1400	1.5925	3.385	570	98
5	15	1350	1.5880	3.305	—	—
15	8	1400	1.5985	3.455	—	—
20	5	1400	1.6028	3.505	—	—
20	10	1250	1.6064	3.515	—	99
10	20	1200	1.5958	3.376	—	93
5	30	1200	1.5981	3.265	—	—
20	20	1150	1.6101	3.512	—	101
10	30	1150	1.5978	3.352	550	—
20	25	1200	1.6112	3.505	540	96
30	20	1100	1.6252	3.650	—	96
20	30	1150	1.6101	3.478	—	95
10	40	1100	1.5937	3.287	—	95
30	25	1100	1.6253	3.640	—	—
20	35	1150	1.6093	3.455	—	—
50	10	1250	1.6614	3.991	—	106
40	20	1100	1.6417	3.802	—	99
30	30	1100	1.6261	3.632	530	94

variety of groups in which both  $\text{BO}_3$  triangles and  $\text{BO}_4$  tetrahedra are present [11]. In the  $\text{BO}_3$  units one or more oxygens are of the non-bridging type, and consequently the tendency of the network to contract is reversed. This explanation for the extremes in physical properties is supported by NMR studies reported by Yun and Bray [10] and the results of laser Raman spectroscopy reported by Konijnendijk [11]. The latter author, however,

concluded that at small  $\text{B}_2\text{O}_3$  contents predominantly metaborate groups ( $\text{B}_3\text{O}_6^{3-}$ ) are formed which contain three non-bridging oxygens (NBO's).

As  $\text{SiO}_2$  replaces  $\text{GeO}_2$  (increasing  $x$ ) the anomalies related to the  $\text{BO}_4$  tetrahedra formation are preserved almost throughout the ternary system, although they become less pronounced. For the K–Ba–borogermanate glass (at  $x + y = 70$ ) the

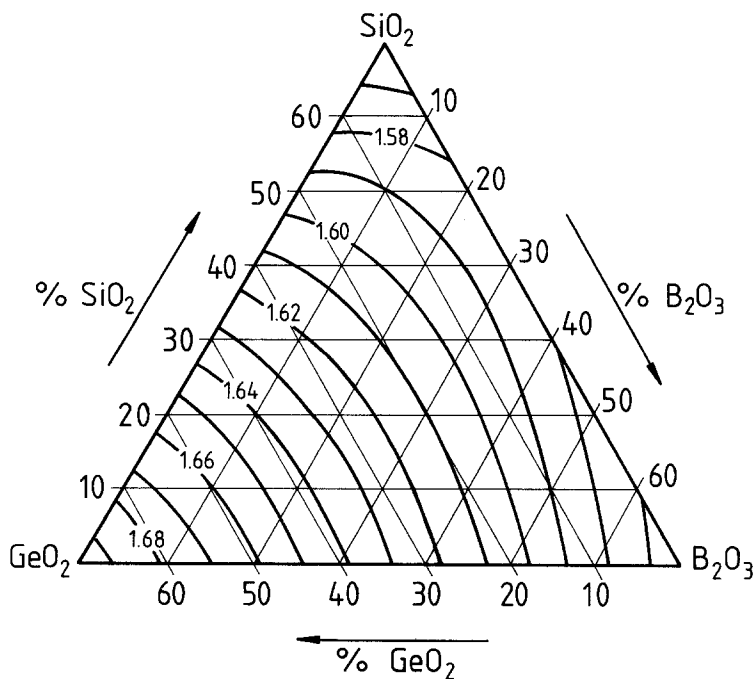


Figure 1 Contour map of refractive index  $n_{\text{D}}$  of  $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot (70-x-y)\text{SiO}_2\cdot x\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  glasses (mol %).

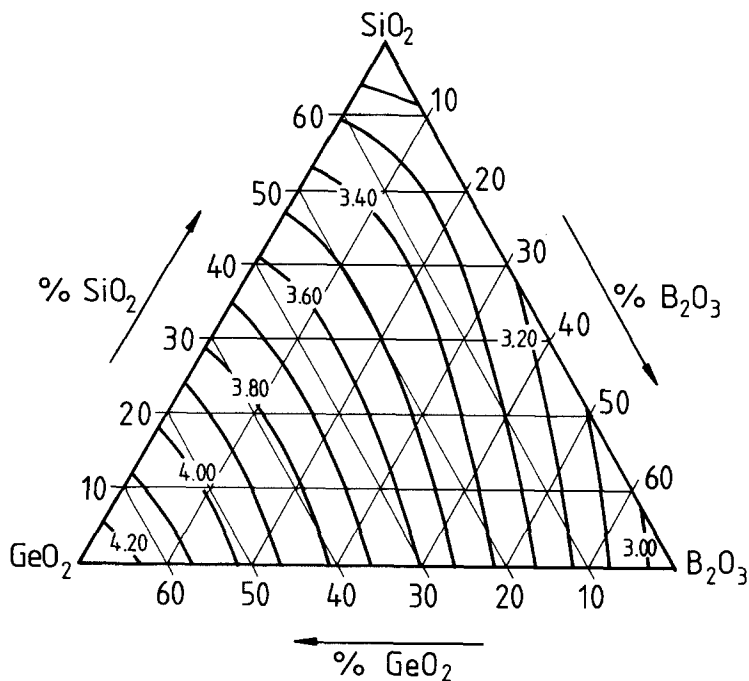


Figure 2 Contour map of density  $D$  ( $\text{g cm}^{-3}$ ) of  $10\text{K}_2\text{O}\cdot 20\text{BaO}\cdot(70-x-y)\text{SiO}_2\cdot x\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  glasses (mol %).

minimum in  $\alpha$  even turns into a slight maximum, while the  $D$  and  $n_D$  anomalies are no longer observed.

The latter effect is caused by the dominating influence of  $\text{GeO}_2$  on both properties, overshadowing effects of boron coordination transformations. In order to investigate to what extent the germanium coordination is affected by  $\text{B}_2\text{O}_3$  introduction,

we calculated the molar refraction  $R_m$  for the two series of comparable glasses  $10\text{K}_2\text{O}\cdot 20\text{BaO}(70-y)\text{SiO}_2\cdot y\text{B}_2\text{O}_3$  (I) and  $10\text{K}_2\text{O}\cdot 20\text{BaO}(70-y)\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  (II) using the Lorenz-Lorentz equations:

$$R_M = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{\bar{M}}{D}$$

where  $\bar{M}$  is the mean molar weight, in this case

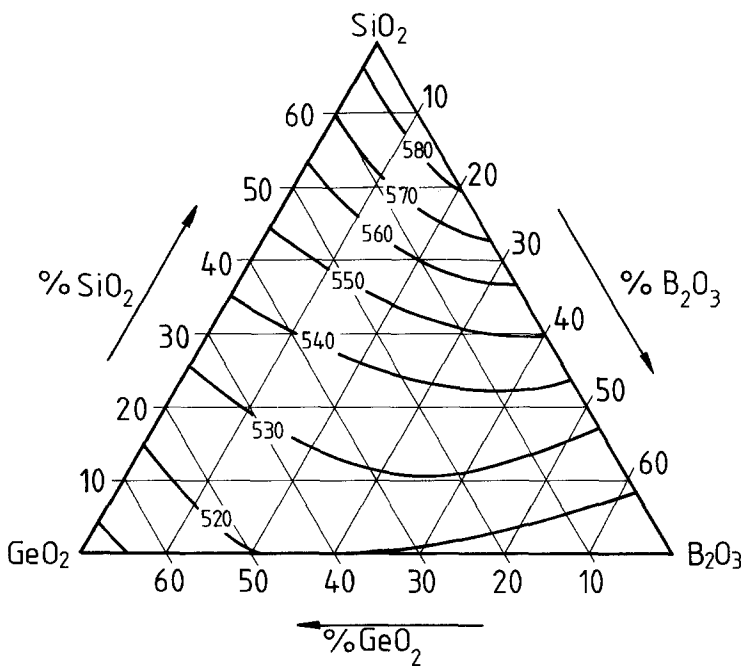


Figure 3 Contour map of transition temperature  $T_g$  ( $^{\circ}\text{C}$ ) of  $10\text{K}_2\text{O}\cdot 20\text{BaO}(70-x-y)\text{SiO}_2\cdot x\text{GeO}_2\cdot y\text{B}_2\text{O}_3$  glasses (mol %).

given by

$$\begin{aligned} \bar{M} &= 0.7M(\text{K}_2\text{O}) + 0.2M(\text{BaO}) \\ &+ (0.7 - x - y)M(\text{SiO}_2) + 0.01xM(\text{GeO}_2) \\ &+ 0.01yM(\text{B}_2\text{O}_3). \end{aligned}$$

$R_m$  is usually considered to be composed additively from the contributions of each type of ion  $i$  in the glass: the ionic refraction  $R(i)$  is proportional to the polarizability of the ion  $i$  and in most cases is independent of glass composition. Only  $R(\text{O}^{2-})$  is significantly smaller for BO's than for NBO's, owing to the higher polarizability of the latter. For instance in *K* germanosilicate glasses  $R(\text{BO}) = 3.70 \text{ cm}^3$  and  $R(\text{NBO}) = 4.43 \text{ cm}^3$  [6]. A comparison of  $R_m$  values for glass systems I and II will reveal differences in the relative number of NBO's and BO's in the two series of glasses. The relative quantities of  $\text{GeO}_4$  tetrahedra and  $\text{GeO}_6$  octahedra can be determined because in the latter units  $\text{Ge}^{4+}$  is coordinated by BO's only.

To compare  $R_m$  of the two series of glasses I and II one has to take the high  $R(\text{Ge}^{4+}) = 2.60 \text{ cm}^3$  compared with  $R(\text{Si}^{4+}) = 0.04 \text{ cm}^3$  [11] into account by subtracting the contribution of  $R(\text{Si}^{4+})$  or  $R(\text{Ge}^{4+})$  from  $R_m$  for glasses I and II, respectively. One obtains for system I:  $R_m^*(\text{I}) = R_m - 0.04(0.70 - 0.01y)$  and for system II:  $R_m^*(\text{II}) = R_m - 2.60(0.70 - 0.01y)$ . Using the  $R_m^*$  values shown in Fig.4 a direct comparison is allowable.

For  $y = 0$ ,  $R_m^*(\text{II})$  is smaller than  $R_m^*(\text{I})$  owing to the presence of  $\text{GeO}_6$  octahedra, coordinated by BO's. According to Verweij and Buster [16] the  $30\text{R}_2\text{O} \cdot 70\text{GeO}_2$  glass ( $y = 0$ ) can be characterized as  $60\text{R}^+ \cdot 66\text{Ge}(4) \cdot 4\text{Ge}(6) \cdot 118\text{BO} \cdot 52\text{NBO}$  and  $30\text{R}_2\text{O} \cdot 70\text{SiO}_2$  as  $60\text{R}^+ \cdot 70\text{Si}(4) \cdot 110\text{BO} \cdot 60\text{NBO}$ . As  $y$  increases, the difference between  $R_m^*$  diminishes and at about  $y = 10$  the two  $R_m^*$ -composition curves are almost identical. This indicates that borogermanate glasses with  $y > 10$  no longer contain any  $\text{GeO}_6$  octahedra. The substitution of a relatively small amount of  $\text{B}_2\text{O}_3$  for  $\text{GeO}_2$  was enough to completely transform the  $\text{GeO}_2$  octahedra, present at  $y = 0$ , into  $\text{GeO}_4$  tetrahedra. At  $y > 10$  the glasses in series I and II have a largely comparable structure.

#### 4. Conclusions

Glass formation is found for every composition in the system  $10\text{K}_2\text{O} \cdot 20\text{BaO} \cdot (70 - x - y)\text{SiO}_2 \cdot x\text{GeO}_2 \cdot y\text{B}_2\text{O}_3$  (mol %). When  $\text{B}_2\text{O}_3$  is substituted for  $\text{SiO}_2$

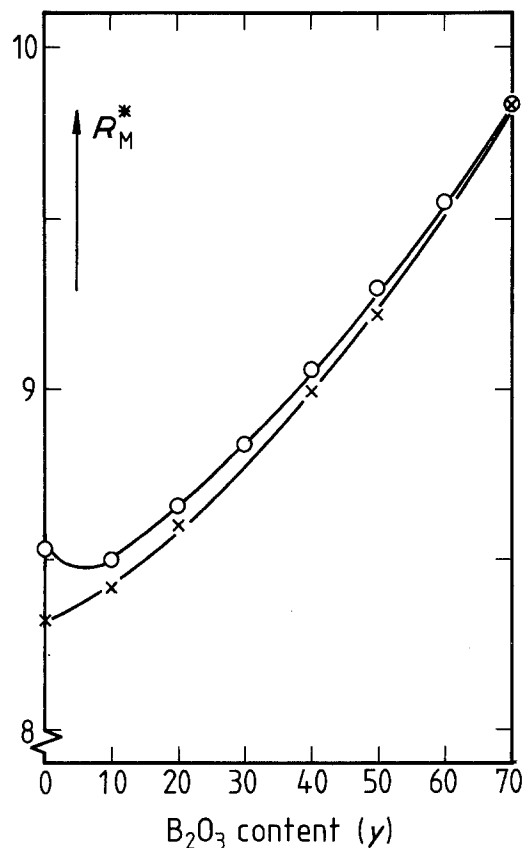


Figure 4 A comparison between  $R_m^*$  for  $10\text{K}_2\text{O} \cdot 20\text{BaO} \cdot (70 - y)\text{SiO}_2 \cdot y\text{B}_2\text{O}_3(0)$  and  $10\text{K}_2\text{O} \cdot 20\text{BaO} \cdot (70 - y)\text{GeO}_2 \cdot y\text{B}_2\text{O}_3(x)$ , respectively, (mol %).

the well-known anomalies in physical properties are observed. Substitution of  $\text{GeO}_2$  for  $\text{SiO}_2$  results in a gradual change in physical properties without any anomalies. The physical properties of glasses with a high  $\text{GeO}_2$  content and low  $\text{B}_2\text{O}_3$  content show that  $\text{GeO}_6$  octahedra are present in these glasses. The  $\text{GeO}_6$  octahedra are completely transformed into  $\text{GeO}_4$  tetrahedra as the  $\text{B}_2\text{O}_3$  content rises above  $y = 10$ .

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