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# Reports of the Academy of Sciences of the USSR

1961

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Figure 1

Figure 1: Figure 1

**Abstract****Full Text****Reports of the Academy of Sciences of the USSR**

1961. Volume 138, No. 1

**PHYSICAL CHEMISTRY****E. M. Rabinovich****ON THE DETERMINATION OF THE CURVES OF FORMATION OF CRYSTALLIZATION CENTERS AND THE RATE OF CRYSTAL GROWTH IN GLASS BY MEANS OF DENSITY MEASUREMENTS***(Presented by Academician A. V. Shubnikov, December 13, 1960)*

The construction of Tammann curves for the dependences of the number of crystallization centers ( $KV$ ) and the linear rate of crystal growth ( $KG$ ) on temperature (<sup>1</sup>) for silicate glasses requires the performance of an extremely laborious investigation. In the case of the formation, under the action of mineralizers, of a finely crystalline structure, such an investigation can be carried out only with the aid of an electron microscope, which makes still more difficult the possibility of practical use of the indicated curves for controlling crystallization.

In the present article are set forth the results of a study of crystallization and a method for constructing curves analogous to  $KV$  and  $KG$ , for glasses containing mineralizers, by density measurements, the value of which depends on the compactness of packing of the substance and, consequently, also on the ratio of the crystalline and glassy phases. For a glass whose composition corresponds to that of a definite chemical compound not undergoing polymorphic transformations, this dependence may be represented by the expression:

**Fig. 1.** Change in the density  $\rho$  of glass I as a result of twofold heat treatment. On the abscissa axis—temperatures of the primary treatment for curve 1 (1 hr; secondary treatment 30 min at 930°) and temperatures of the secondary treatment for curves 2 and  $\sqrt[3]{\Delta\rho}$  (1 hr; primary treatment 1 hr at 750°)

$$\Delta\rho = \rho - \rho_c = (\rho_k - \rho_c)p, \quad (1)$$

where  $\rho$  is the density of the substance whose degree of crystallization (in volume fractions) is equal to  $p$ ;  $\rho_c$  is the density of the substance in the glassy state;  $\rho_k$  is the density of the substance in the crystalline state;  $\rho_k > \rho_c$  <sup>(2,3)</sup>.

It is easy to show that

$$p = kl^3n, \quad (2)$$

where  $l$  is the mean linear size of a crystal;  $n$  is the number of crystals per unit volume;  $k$  is a constant depending on the shape of the crystals.

In the case of complex glasses the value  $\rho_k$  is a weighted mean of the densities of all crystalline phases, in connection with which expression (1) can be applied to these glasses if the degree of crystallization is sufficiently large (of the order of 0.3-0.5).

For the investigation, multicomponent aluminosilicate glasses synthesized at the Electrotechnical Institute were selected: I ( $\rho_c = 2.610 \text{ g/cm}^3$ ) and II ( $\rho_c = 2.875 \text{ g/cm}^3$ ), containing  $\text{TiO}_2$  as a

of the mineralizer, and photosensitive glass III ( $\rho_c = 2.360 \text{ g/cm}^3$ ), containing small additions of silver. The lowest temperatures at which external signs of crystallization appear in these glasses are as follows: glass I,  $830^\circ$ , 1-8 h; glass II,  $930^\circ$ , 1 h,  $900^\circ$ , 4 h,  $850^\circ$ , 8 h; glass III,  $550\text{-}600^\circ$ , 1-2 h (depending on the irradiation).

The density was determined by the method of hydrostatic weighing on an analytical balance. Glass specimens, in a number of not less than 3 for a single determination, were subjected to double heat treatment <sup>(1)</sup>. The purpose of the primary treatment, after which no external signs of crystallization were observed in the specimens, was the formation of invisible crystallization centers; the purpose of the secondary treatment was their growth.

**Fig. 2.** Change in the density  $\rho$  of glass I as a function of the time of the primary ( $750^\circ$ ) and secondary ( $930^\circ$ ) heat treatment

In Fig. 1 are shown curves of the change in the density of glass I after crystallization with a constant temperature of the secondary heat treatment (curve 1), corresponding to the temperature of the maximum of the first exothermic effect on the thermogram ( $930^\circ$ ), and with a constant temperature of the primary treatment (curves 2,  $\sqrt[3]{\Delta\rho}$ ); the time of both treatments is constant for a given curve. If it is assumed that the average sizes of the crystals do not depend on the conditions of the primary treatment, then each value of  $\rho - \rho_c$  on curve 1 is proportional, according to (1) and (2), to the number of crystallization centers per unit volume, i.e., curve 1 is analogous to  $KV$ ; each value on curve 2 is

proportional to the average volume of a crystal, and on the curve  $\sqrt[3]{\Delta\rho}$ —to the average length (or growth rate) of a crystal, i.e., the curve  $\sqrt[3]{\Delta\rho}$  is analogous to  $KG$ .

However, the condition that the crystal sizes be independent of the conditions of the primary treatment, i.e., of the number of centers per unit volume, is fulfilled only for not very high degrees of crystallization, when each crystal is located sufficiently far from its neighbor. This must especially be taken into account for glasses in which the crystallization centers are situated at distances on the order of 1–2  $\mu$  from one another.

The curves in Fig. 2 make it possible to verify that the conditions of the preceding experiment were chosen correctly. If the treatment time at 930° does not exceed 1.5 h, then doubling the duration of the primary treatment at 750°, and hence doubling the number of crystallization centers, corresponds to a doubling of the difference  $\rho - \rho_c$ .

**Fig. 3.** Change in the density  $\rho$  of glass II as a result of double heat treatment. Primary treatment 1 h; secondary treatment: 1–1 h at 850°; 2–2 h at 850°; 3–30 min at 950°

With a longer time of secondary treatment...

of treatment this proportionality is disturbed, and the condition for the correct construction of curves analogous to  $KV$  and  $KG$  is not satisfied.

Fig. 3 shows that incorrectly chosen conditions for the secondary treatment of glass II, which ensure an excessively high degree of crystallization, lead to a change in the shape of curves 2 and 3 as compared with curve 1, and also to a shift of the maximum.

Fig. 4 gives a curve of the change in density, analogous to  $KV$ , for glass III, previously irradiated with ultraviolet rays. The first crystalline silicate phase separating in this glass is  $\text{Li}_2\text{SiO}_3$ . Its crystallization centers are apparently the finest silver crystallites formed still earlier<sup>(4)</sup>; at a lower temperature of secondary treatment (500–550°) they produce colloidal coloration of the glass without crystallization of the main phases. The primary temperature to which the maximum intensity of coloration corresponds agrees with the temperature of the maximum on the density-change curve (Fig. 4). This agreement, like the agreement between the temperature of the maximum of curve 2 ( $\sqrt[3]{\Delta\rho}$ ) for glass I (Fig. 1) and the temperature of the maximum crystallization effect on the thermogram (930°), confirms the validity of using density measurements for the quantitative evaluation of crystallization in glasses containing mineralizers.

**Fig. 4.** Change in density  $\rho$  of irradiated glass III as a result of two-stage heat treatment. Primary treatment 1 hour; secondary treatment 30 min at 720°.

The magnitudes of the areas under curves of the type of curves 1 and 2 in Fig. 1 are the same ( $\text{g} \cdot \text{deg}/\text{cm}^3$ ); therefore they may conventionally characterize the crystallization capacity of the glass. To introduce a correction for the formation

Fig. 4. Change in density  $\rho$  of irradiated glass III as a result of two-stage heat treatment. Primary treatment 1 hour; secondary treatment 30 min at 720°

Figure 2: Fig. 4. Change in density  $\rho$  of irradiated glass III as a result of two-stage heat treatment. Primary treatment 1 hour; secondary treatment 30 min at 720°

and growth of new centers at the temperatures of secondary treatment, these areas should be bounded below by the curves of density values of samples subjected only to secondary treatments, without primary ones. For glass I this gives values equal to or somewhat smaller than  $\rho_c$  (2.609 g/cm<sup>3</sup> after 4 hours at 930°, 2.612 after 8 hours). These curves are also, to a certain extent, a correction to expression (1).

The curves of Fig. 2 and calculations by (1) and (2) make it possible to establish the kinetics of the decrease in the linear growth rate of crystals, caused by the low rate of diffusion, with time at a constant number of crystallization centers.

Density measurements can also be used to study the influence of irradiation conditions on photosensitive glass under constant heat-treatment conditions.

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Received  
29 XI 1960

## CITED LITERATURE

1. G. Tammann, *The Glassy State*, Moscow-Leningrad, 1935.
2. G. G. Sentyurin, *Transactions of the Moscow D. I. Mendeleev Institute of Chemical Technology*, **19**, 178 (1954).
3. S. I. Silvestrovich, E. M. Rabinovich, *Journal of the All-Union Chemical Society named after D. I. Mendeleev*, **5**, 2, 186 (1960).
4. S. D. Stookey, *Glastechn. Ber.*, Sonderband V, Intern. Glaskongreß, **32 K**, 5, 1959, S. 1.

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