CRYSTALLIZATION OF MELTS AND GLASSES IN THE SYSTEM $MgO-Al_2O_3-SiO_2$ WITH $ZrO_2 + TiO_2$ NUCLEANTS

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Most of the melts and glasses investigated crystallized in volume during heat treatment up to 1000 °C. The tendency to metastable separation, which precedes crystallization, increases with increasing MgO/Al_2O_3 *ratio. The course of crystallization of the* ZrO_2 *phase,* Mg *petalite, solid solutions of* β*-quartz and enstatite depends on initial composition, way of treatment and crystallization temperature.*

Increasing crystallization temperature brings about decomposition of Mg *petalite and precipitation of* β*-quartz solid solutions. The composition region of metastable* Mg *petalite was determined by means of X-ray diffraction analysis.*

INTRODUCTION

The system $MgO-Al_2O_3-SiO_2$ comprises, in addition to the 11 known stable compounds (some of which may form solid solutions), also several metastable phases: solid solutions of β-quartz [1], osumilite [2] and Mg petalite [2], [3].

During heat treatment of glasses and melts, these crystalline phases may precede precipitation of stable phases and up to certain temperatures they may survive even for considerably long periods of time.

Heat treatment of three-component glasses in this system results in surface crystalization only. Volume crystallization of suitable phases can only be accomplished with the use of nucleating agents. This method has been employed in the preparation of glass-crystalline materials of advantageous properties, e.g. on the basis of solid solutions of β-quartz., α-cordierite, enstatite.

The chemical composition of Mg petalite is not yet known; crystallographic data and the conditions of its formation and transformation frequently differ. For this reason petalite has been paid special attention in the present study.

The region of assumed composition of Mg petalite according to Schreyer and Schairer [2] differs from the composition considered by Varshal [4]. Both these regions are shown in Fig. 1. They are three-component composition regions where $MgO/Al_2O_3 > 1$. However, with glasses containing ZrO_2 as nucleant, Holmquist [3] and Conrad [5] succeeded in obtaining Mg petalite even from compositions in which the ratio MgO/Al_2O_3 was equal to unity. Solid solutions of β-quartz and enstatite precipitated in most of the instances simultaneously with Mg petalite.

According to the results of Varshal [6] — [8], three-component glasses and TiO_2-nucleated glasses, in which the MgO molar content was higher that the Al_2O_3 one, were subject to metastable separation which preceded crystallization and affected precipitation of the crystalline phases. On the other hand, with ZrO_2-nucleated glasses Neilson [13] has found no closer relation between metastable separation and the crystallisation mechanism.

In the available literature, crystallisation has been brought about by heating

the base glasses within the T_g to T_L temperature range. According to the data in [9] — [11] there is a possibility of achieving volume crystallization and creating glass ceramics by controlled cooling of melts.

The present study had the aim to follow phase transformations up to 1000 °C for compositions in which the ratio $MgO/Al_2O_3 > 1$. The nucleating agents employed were 6 mol. % ZrO_2 + 3 mol % TiO_2 in all the compositions examined. Crystallization was effected mostly by cooling the melts down to crystallization temperature, and in some instances (for the sake of comparison) also by heating the glasses up to the crystallization temperature region.

EXPERIMENTAL

Composition and preparation of the glasses

As all the glasses in question contained the same amounts of ZrO_2 and TiO_2, they are further on designated only according the molar percent content of the basic components (e.g. 60/10/30 = 60 % SiO_2, 10 % Al_2O_3, 30 % MgO).

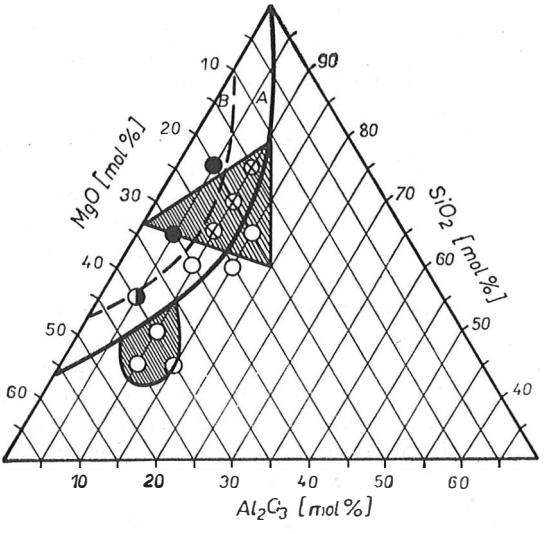


Fig. 1. Composition of the examined melts and glasses in a three-component diagram, in mol %;
○ clear glasses, ⊗ opalescent glasses, ● white opaque glasses, ◑ glass separated into two layers; A — metastable separation region according to Varshal [6], *B — region of glasses separated on cooling, according to Varshal* [6]. *The regions marked in the diagram are the regions of assumed Mg petalite composition* ([2] *and* [4]).

Phase transformations in the course of heat treatment were studied on 12 different compositions, which are plotted in Fig. 1. The diagram shows that both regions considered for Mg petalite composition are covered by the composition range selected.

The glasses were melted from pure or A. R.— grade raw materials; ground and refined rock quartz was used as the siliceous component. The materials were melted in PtRh crucibles in an electric furnace under the following conditions:

glass charge	100 to 500 g
melting temperature	1550 to 1620 °C (according to composition)
time of melting	7 to 10 hours.

The melt was agitated several times during melting in order to ensure its homogeneity. After melting the material was cast into the form of rods in a steel grate.

Heat treatment

In the case of melt crystallization, 6.5g of the glass was first remelted in a Pt boat above the liquidus temperature for a period of 20 minutes. The boat was then quickly transferred into the isothermic zone of another tube furnace heated at the crystallization temperature. After the required period of time the boat with sample was removed and cooled down in air. The rapid transfer into another furnace ensured stepless cooling down of the melt to its crystallization temperature, as has been verified by direct measurement. Equalization of the required crystallization temperature in the sample was achieved within about 2 minutes.

In the case of glass crystallization a 6.5g sample in a Pt boat was placed in the same crystallization furnace heated at the required treatment temperature, and then cooled in air.

The heat treatment temperatures were varied in the range of 800 to 1000 °C; the time of crystallization was in both cases counted from the moment of placing the sample in the isothermic zone of the crystallization furnace.

X-ray diffractometry

The measurements were carried out on powdered samples ground under identical conditions, using the Rigaku-Denki diffractograph with monochromatic CoK_α radiation, scanning region $\Theta = 5$ to 30 deg.

For identification of the precipitated phases the determined d-spacings and relative intensities I/I_0 were compared with ASTM standards.

The heights of the main diffraction peaks of precipitated phases were determined as a measure of their relative content.

Differential thermal analysis was carried out on the Netzsch apparatus. The sensitivities employed were 1 mV and 0.05 mV, the heating rate 10 °C/min and 2 °C/min respectively. The ground samples had a grain size of 0.3 to 1 mm.

Metastable separation

Some of the glass samples exhibited metastable liquid separation, taking place during the cooling of the homogeneous melt down from its melting temperature. The critical immiscibility temperature of some samples was

high, e.g. with 65/10/25 it amounted to 1150 °C. In these cases the samples cast into the form of rods (3 to 7 mm in thickness) were whitish in colour or opaque. Phase separation could only be suppressed by extremely rapid quenching of small amounts of melt.

In the ternary diagram in Fig. 1 the compositions examined are plotted together with specification of sample appearance after air cooling. As implied by this Figure, the tendency to separation decreases with increasing Al_2O_3 content at both constant MgO content (glasses 75/5/20, 70/10/20/, 65/15/20), and identical SiO_2 content (glasses 65/5/30, 65/10/25, 65/15/20).

For comparison, the diagram in Fig. 1 further shows the region of metastable separation for the three components and 1000 °C and the boundaries of three-component compositions separating on cooling according to Varshal [6]. A comparison of these results with our experimental ones shows that addition of the nucleants employed broadens somewhat the region of compositions separating in the course of cooling.

Characteristics of the precipitated crystalline phases

The following crystalline phases were determined by X-ray diffraction analysis in the crystallized samples: a ZrO_2 phase, Mg petalite, solid solutions of β-quartz, enstatite.

In view of the low ZrO_2 content in the glasses, only higher intensity diffraction peaks could be identified in the compositions in question. Their width, in particular at the beginning of crystallization, allows to assume a very small size of crystals of this phase or a considerable degree of nonuniformity in the crystalline structure.

The experimentally determined values d and relative intensities I/I_0 for the ZrO_2 phase are listed in Table I.

Table I

The results of X-ray diffraction analysis of the ZrO_2 phase

d(Å)	I/I_0
2,92	100
2,53	21
1,80	21
1.51	14
1.46	17

A comparison of the experimental values with tabellated data on known zirconium compounds has shown that very similar values d and I/I_0 are exhibited by several phases, namely tetragonal ZrO_2, solid solutions of ZrO_2 with cubic or tetragonal lattice, and $ZrTiO_4$.

Since the values determined for the main diffraction maxima did not permit their explicit identification, this crystalline phase is further called "the ZrOt phase".

In literature [3], [5] where ZrO_2 was likewise used as nucleant of volume

crystallization, the ZrO_2 phase is designated as "ZrO_2 solid solutions with a tetragonal or cubic lattice".

Some compositions contained, after their crystallization, considerable amounts of Mg petalite which constituted the main phase and coexisted only with the ZrO_2 phase.

Evaluation of X-ray diffraction spectra of the crystallized samples yielded for Mg petalite the d and I/I_0 values listed in Table II, columns A and B. Column A pertains to Mg-petalite precipitated from glass containing 5 to 10 mol % Al_2O_3. The composition which was closer to the connecting line SiO_2 — MgO . Al_2O_3, i.e. that for $MgO/Al_2O_3 = 1$, containing 15 mol % Al_2O_3, yielded Mg petalite with somewhat different d and I/I_0 values, which are listed in column B. Table II also lists literary X-ray data for Mg petalite.

Table II

The results of X-ray diffraction analysis for Mg petalite

Schreyer and Schairer [2]		Holmquist [3]		Values measured			
d [Å]	I/I_0	d [Å]	I/I_0	d [Å]	A I/I_0	d [Å]	B I/I_0
7.2	8	7.17	8	7.1	7	7.02	11
4.08	8	—	—	—	—	—	—
3.79	20	3.74	100	3.75	8	3.69	100
3.69	100	3.66	90	3.66	100	3.63	95
3.58	25	3.56	15	3.55	17	3.54	22
—	—	2.66	4	—	—	—	—
2.55	11	2.54	8	2.59	5	2.54	7
2.47	8	2.45	3	—	—	—	—
2.39	8	2.38	5	—	—	—	—
—	—	2.10	2	—	—	—	—
1.95	6	2.05	9	2.05	7	2.04	10
1.90	5	1.91	3	1.91	6	1.91	7

The comparison shows that similar differences in d and I/I_0 of Mg petalite also arise in the results by Schairer [2] and Holmquist [3]. The ratio MgO/Al_2O_3 in the initial glass was larger than unity in study [2] and equal to unity in study [3].

The course of crystallization in terms of temperature and composition

The time of heat treatment was 30 minutes with all the samples. The crystallization was effected by cooling the melts down to crystallization temperature. Apart from composition 45/15/40 all the melts investigated crystallized in volume after having been cooled down to the respective suitable temperature of max. 1000 °C. The formed crystalline phases were determined in the crystallized products by of X-ray diffraction. The height I of the main diffraction peak of each phase was used as an index of its relative amount. The results are summarized in Fig. 2.

Crystallization of the ZrO_2 phase

The ZrO_2 phase precipitated at both the lowest and the highest crystallization temperatures with all the compositions. The amount of this phase increases proportionally with crystallization temperature. As indicated by Fig. 2 e.g. on compositions 45/10/45 and 60/10/30, the ZrO_2 phase precipitates at lower

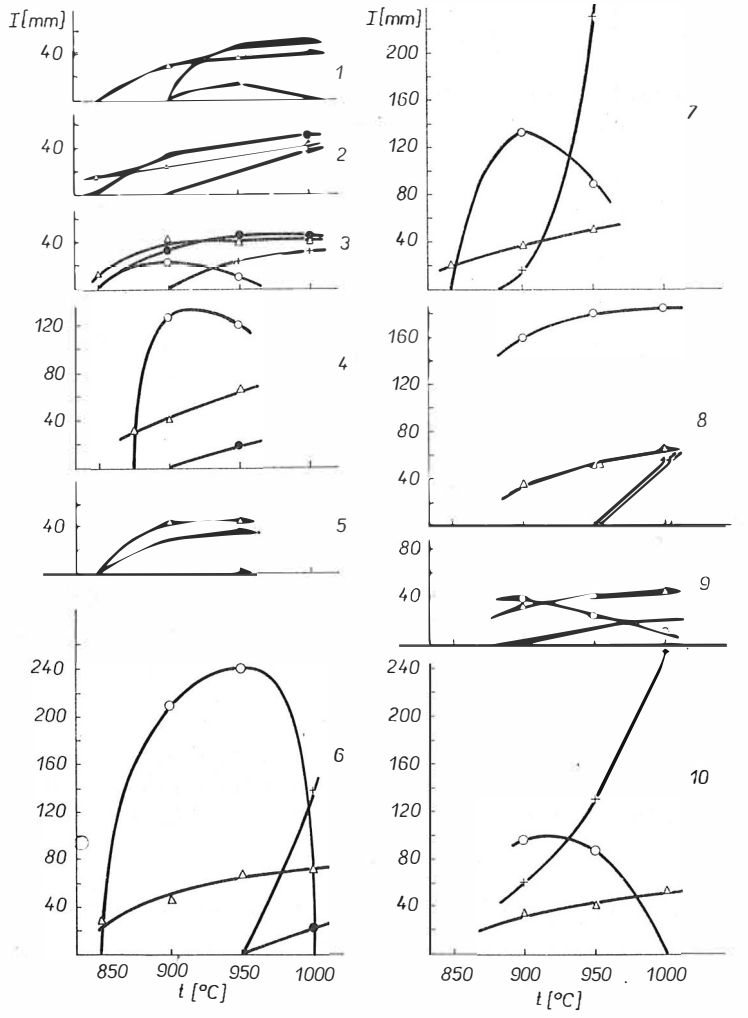


Fig. 2. The course of precipitation of crystalline phases in terms of melt crystallization temperature and composition. Time of treatment 30 minutes. Composition of melts in mol % $SiO_2/Al_2O_3/$ MgO:

1 — 45/10/45 *2 — 45/15/40* *3 — 50/10/40*
4 — 60/10/30 *5 — 65/5/30* *6 — 65/10/25*
7 — 65/15/20 *8 — 70/10/20* *9 — 75/5/20* *10 — 75/10/15*

Δ ZrO_2 *phase,* ○ Mg *petalite,* ● *enstatite,* + *solid solutions of* β*-quartz.*

temperatures than the other crystalline phases. In agreement with the results of study [12] it can be stated that ZrO_2 phase is the first crystalline phase in the compositions investigated.

Crystallization of Mg petalite

According to the results in Fig. 2, Mg petalite is the main crystalline phase in the material containing 10 to 15 % Al_2O_3 and more than 50 % SiO_2.

The temperature dependence of precipitation for this phase is similar with most of the compositions in question. The amount of Mg petalite first increases to a maximum with increasing temperature, and then decreases. The decrease of Mg petalite content is accompanied by an increase in the content of β-quartz solid solutions; with some compositions (65/10/25) also enstatite is formed at higher temperatures. A comparison of the results in Fig. 2 further suggests that the crystallization temperatures at which the maximum Mg petalite

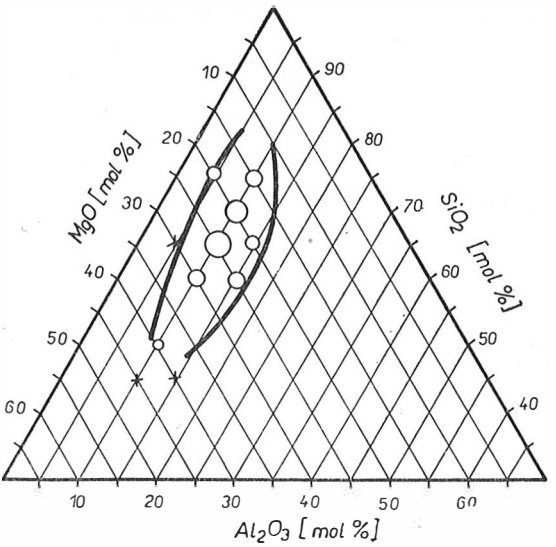


Fig. 3. Metastable existence region of Mg *petalite;*
○ *composition yielding* Mg *petalite by crystallization,* × *composition at which* Mg *petalite was not determined.*

content was achieved, increase with increasing SiO_2 content in the initial material. The height of this temperature is likewise affected by the molar ratio MgO/Al_2O_3 in the initial material. The results in Fig. 2 (e.g. compositions 70/10/20 and 75/10/15) indicate that with MgO/Al_2O_3 approaching unity there increases the tendency of the melt to crystallization of β-quartz solid solutions.

Analyses of the phase compositions of heat treated samples allow to determine approximately the composition range of melts yielding Mg petalite during crystallization. This region is plotted in Fig. 3, and the relative quantitites for the individual compositions are distinguished by the size of the dots.

The highest content of Mg petalite was determined in samples prepared by crystallization of the melt 65/10/25. The kinetics of volume crystallization of this phase was studied in detail in [12]. The maximum crystallization degree attained the value of 0.72 at a crystallization temperature of 950 °C.

Crystallization of β-quartz solid solutions

Solid solutions of β-quartz do not crystallize from the material containing 5 mol. % Al_2O_3. According to the results in Fig. 2, with the exception of composition 45/10/45, the amount of this phase increases with temperature. The onset of crystallization is shifted towards higher temperatures when compared with Mg petalite.

The increase in the content of β-quartz solid solutions mostly involved a decrease in the content of Mg petalite. An increasing content of the former was noted in relation to a shift of the initial melt composition towards the SiO_2-MgO . Al_2O_3 line, i.e. closer to the composition of the crystals of this phase. This tendency is indicated in Table III. With most of the compositions

Table III

Relative amounts of β-quartz solid solutions in terms of melt composition

Composition [mol. %]	MgO/Al_2O_3	Main diffr. peak intensity	Crystalliz. temperature [°C]
45/10/45	4.50	12	950
50/10/40	4.00	34	1000
65/10/25	2.50	139	1000
70/10/20	2.00	57	1000
75/10/15	1.50	264	1000
65/15/20	1.33	230	950

the highest content of β-quartz solid solutions was found at 1000 °C with the exception of compositions 45/10/45 and 65/15/20 where the temperature was 950 °C.

As shown by Table III, β-quartz solid solutions crystallized even in compositions considerably far from the SiO_2-MgO . Al_2O_3 line. This can be explained so that crystalization is preceded by metastable liquid separation, where composition of separated liquid phases differs from that of the initial melt above the critical immiscibility temperature. Separation taking place before crystallization was proved by electron microscopy in study [12], and in the case of TiO_2-containing glasses in studies [7], [8].

The course of enstatite precipitation

The pyroxen crystalline phase was the main crystalline product in low-silicate compositions (up to 50 % SiO_2) and in those of 5 % Al_2O_3 content (Fig. 2, composition 65/5/30). The amount of enstatite increased with increasing temperature of crystallization.

A comparison of phase compositions of samples with 10 % Al_2O_3 (Fig. 2) suggests that the amount of precipitated enstatite decreases with increasing SiO_2 content and the onset crystallization temperatures of this phase increase simultaneously. Similarly to the case of β-quartz solid solutions, enstatite was precipitated even from compositions quite removed from the existence region of this phase, as for example composition 75/5/20 at 1000 °C. This composition exhibited a strong tendency to liquid separation (Fig. 1).

A comparison of the courses of crystallization between melt and glass

Composition 65/10/25 was employed for this purpose. The temperatures and time of crystallization were the same for samples prepared by cooling the melt, as for those prepared by heating the glass to the crystallization temperature. Use was made of glass separated by casting the melt into the form of dia. 8 mm rods and their free cooling in air, and of unseparated glass obtained by rapid quenching of small amounts of melt. After appropriate heat treatment the samples were subjected to X-ray diffraction analysis. The results and crystallization conditions are listed in Table IV.

Table IV

Comparison of melt and glass crysrallization 65/10/25 composition. Time of crystallization 30 min.

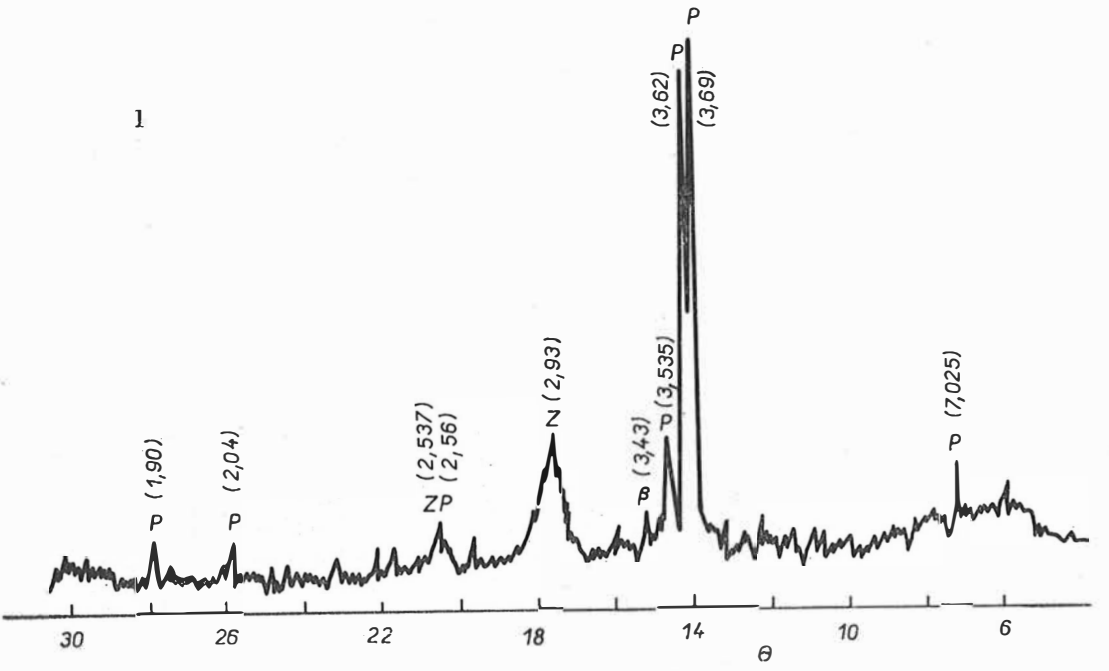
Initial state	Crystallization [°C]	Crystalline phase, main peak intensity in mm
Clear glass	900 950	ZrO_2 — 21 ZrO_2 — 33, Mg pet. — 187 β-quartz solid solution — 22
Separated glass	900 950	ZrO_2 — 25, Mg pet. — 30 ZrO_2 — 38, Mg pet. — 226 β-quartz solid sol. — 8
Melt	900 950	ZrO_2 — 44, Mg pet. — 210 ZrO_2 — 68, Mg pet. — 240

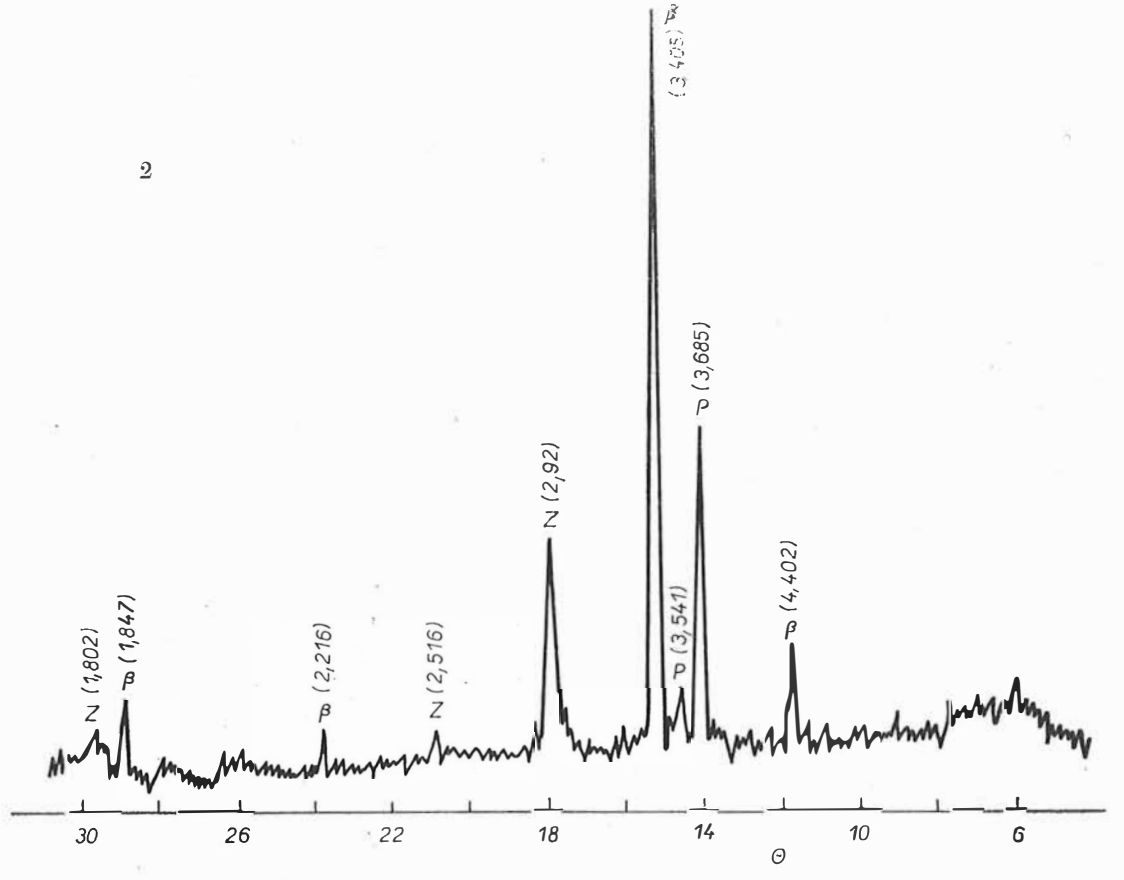
The results in the Table indicate that the same phases are precipitated in the crystallization of both melt and glass. Only in the case of glasses crystallized at 950 °C there was an additional minority content of β-quartz solid solutions.

On the other hand, the mutual differences in the amount of phases precipitated from melt and glass suggest that crystallization proceeds at its highest rate in melt, and at a higher rate in separated glass.

Stability of Mg petalite

Examination of the course of crystallization in terms of temperature (Fig. 2) showed that a decrease in the content of Mg petalite was in most cases accompanied by precipitation of β-quartz solid solutions.


1
P
P
P
(3,62)
(3,69)
(1,90)
(2,04)
(2,537)
(2,56)
N (2,93)
(3,43)
P (3,535)
(7,025)
P
P
ZP
β
30
26
22
18
14
10
6
Θ


2
(3,405)
N (1,802)
β (1,847)
β (2,216)
N (2,516)
N (2,92)
P (3,685)
P (3,541)
β (4,402)
30
26
22
18
14
10
6
Θ

However, enstatite was also precipitated from composition 65/10/25. The following measurement was carried out in order to verify the assumption that high-temperature decomposition of petalite involves crystallization of β-quartz solid solutions.

A low-temperature crystallization product containing considerable amounts of Mg petalite was reheated at a higher temperature where it is already unstable. The final phase composition was determined by X-ray diffraction analysis. The results are listed in Table V, an example of powder diffraction patterns is shown in Fig. 4.

Table V

Decomposition of Mg petalite at higher temperature

Initial sample			Final sample		
Treatment temperature and time	Crystalline phase	I [mm]	Treatment temperature and time	Crystalline phase	I [mm]
65/10/25 crystallized glass 950 °C/30 min.	Mg petalite ZrO_2 phase β-quartz.	226 38 8	1030 °C 30 min.	Mg petalite β-quartz ss. ZrO_2 phase enstatite	85 61 44 15
65/15/20 crystallized melt 900 °C/30 min.	Mg petalite ZrO_2 phase β-quartz ss.	133 37 16	980 °C 90 min.	β-quartz ss. Mg petalite ZrO_2 phase	193 83 56

According to these results, Mg petalite as a low-temperature crystallization product becomes unstable when heated at higher temperatures, decomposes and there arise solid solutions of β-quartz as phases more stable at the given temperature. If the crystallization is preceded by separation, then at low temperatures Mg petalite crystallizes from one liquid phase, while at higher temperatures solid solutions of β-quartz are formed. The second separated phase is probably a source of enstatite, as implied by a comparison of the phase composition of crystallized samples in Fig. 2 for the composition of 10 % Al_2O_3 and 45 to 75 mol % SiO_2.

Differential thermal analysis

The conditions of formation and transformation of Mg petalite were also investigated by means of DTA on glass 65/10/25, at first at a heating rate of 10 °C/min. The DTA record shown in Fig. 5 yielded T_g = 712 °C, the first exothermic peak onset T_1 = 820 °C, the second peak T_2 = 1030 °C.

Fig. 4. A part of X-ray diffraction patterns. Base glass composition 65/15/20. 1 — melt crystallization at 900 °C, 30 minutes, 2 — change in phase composition of sample due to exposure of sample 1 to 980 °C for 90 minutes, P — Mg petalite, Z — ZrO_2 phase, β — β-quartz solid solution.

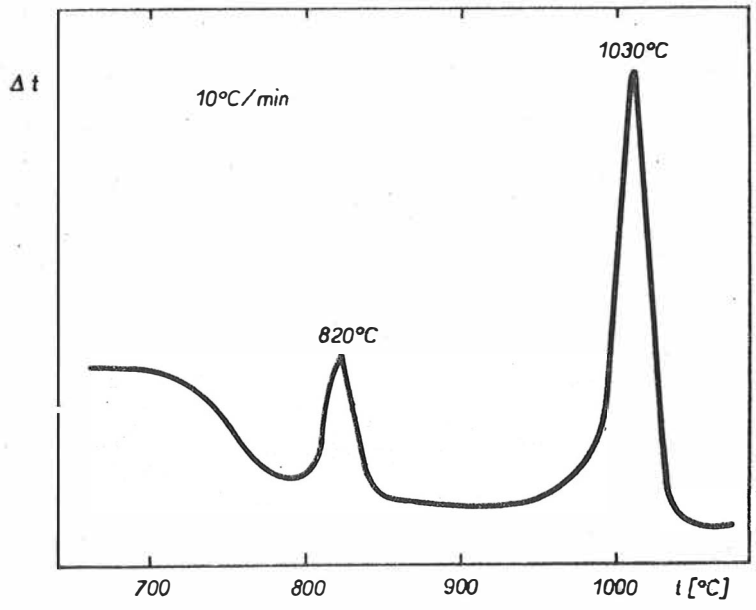


Fig. 5. DTA of glass, composition 65/10/25, heating rate 10 °C/min.

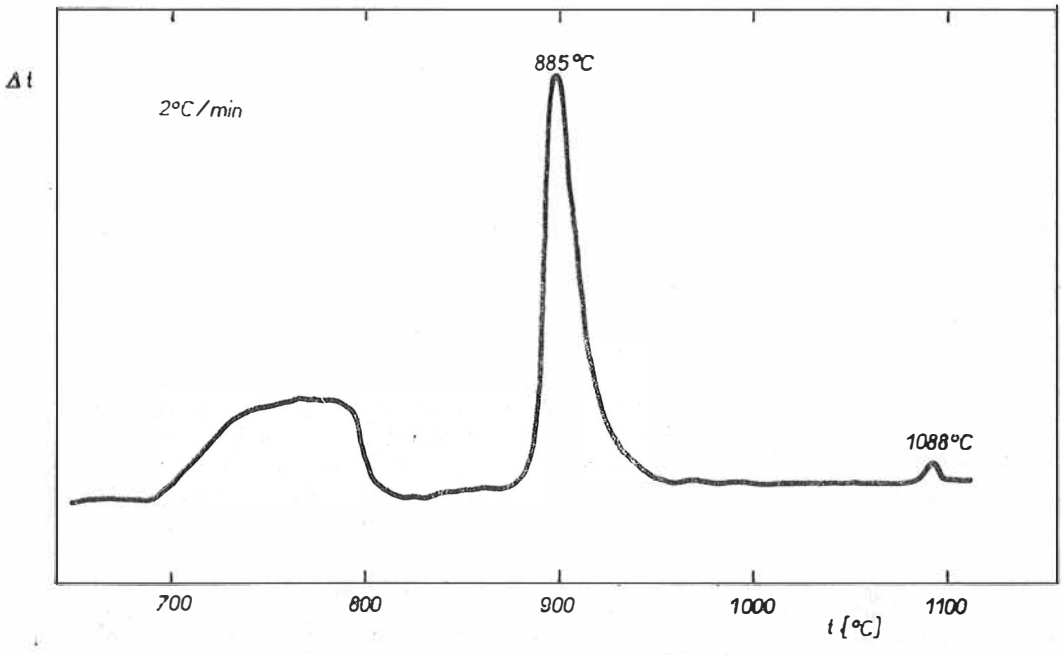


Fig. 6. DTA of glass, composition 65/10/25, heating rate 2 °C/min.

X-ray diffraction analysis showed the first DTA peak to correspond to crystallization of the ZrO_2 phase, the other peak to crystallization of β-quartz solid solutions and enstatite. Immediately after attaining 1030 °C, only the ZrO_2 phase was determined. This means that at a glass heating rate of 10 °C/min Mg petalite cannot form and at temperatures of about 1000 °C there crystallize directly solid solutions of β-quartz, and enstatite.

The DTA measurement was therefore repeated at a heating rate of 2 °C/min. The DTA record is shown in Fig. 6. X-ray diffraction analysis has shown that the first minor thermal changes at 710—820 °C correspond to gradual precipitation of the ZrO_2 phase, the main exothermic peak with its onset at 885 °C corresponding to crystallization of Mg petalite. The minor high-temperature peak in Fig. 6 probably pertains to precipitation of β-quartz solid solutions after previous decomposition of Mg petalite, or crystallization of enstatite.

The heating rate of 2 °C/min is therefore sufficient for the crystallization of Mg petalite.

DISCUSSION

The transformation of Mg petalite to β-quartz solid solutions observed in the present study is in agreement with the results by Holmquist [3] and Conrad [5]. The increasing amount of Mg petalite with increasing SiO_2 content up to 65 mol. % within the region shown in Fig. 3, and the simultaneously decreasing enstatite content in crystallized products allow to assume that the composition of Mg petalite belongs to the higher-siliceous region, as suggested by Schreyer and Schairer [2].

The samples corresponding to the assumed region according to Varshal [4] contained enstatite as the main phase.

Precise determination of Mg petalite was complicated by the fact that the compositions from which it crystallized in larger amounts separated prior to crystallization, in agreement with the results by Varshal [6], [7].

The composition of the separated liquid phases is unknown; however, according to the results of our measurements, Mg petalite and β-quartz solid solutions at higher temperatures should precipitate from a liquid phase having a higher SiO_2 content.

The second separated phase with a lower SiO_2 content may be the source of enstatite.

Varshal, on the other hand, assumes that the low-siliceous separated phase is the source of Mg petalite. Some of the disagreements may be due to different effects of ZrO_2 (used in [4], [5] and in the present study) on separation and nucleation (in particular on the composition of the separated phases) when compared to the effect of TiO_2 employed as nucleator in Varshal's work.

The differences in d and I/I_0 of Mg petalite in Table II for crystallized samples of various compositions suggest that the substance is probably a solid solution. It is interesting that similarly to β-quartz solid solutions, there were prepared samples containing Zn petalite and composed, MgZn petalite [10], [14], [15], [16].

From the point of view of properties these phases are interesting in that by gradual substitution of MgO with ZnO in the initial composition the glass crystalline materials exhibit a continuous decrease of thermal expansivity

from $\alpha = 36$ to 46×10^{-7}/°C for Mg petalite-based materials down to $\alpha \sim 0$ when MgO is totally replaced by ZnO.

The differences in the crystallization rates of melt and glass are probably due to the fact that nucleation begins already during the cooling down of the melt to the crystallization temperature [12], [16].

The differences observed in the rates of transformation between separated and unseparated glass, obtained by different cooling rates, are probably the result of a similar effect.

As the precipitated crystalline phases were identical in both types of glass, heating up of primarily unseparated glass to crystallization temperature probably again brings about separation preceding the crystallization proper.

CONCLUSION

Most of the melts and glasses investigated crystallize in volume. It is possible to utilize single-stage treatment without tempering in the regions where nucleation alone prevails. The crystallization rate of melt is higher than that of glass of the same composition at the same crystallization temperature. The ZrO_2 phase (first crystalline phase), Mg petalite, β-quartz solid solutions and enstatite crystallize in that order at up to 1000 °C. The course of their precipitation depends on temperature and initial composition. Mg petalite is decomposed at increasing temperatures, and β-quartz solid solutions are precipitated.

The composition of Mg petalite is in the higher-siliceous region of about 65 to 75 mol % SiO_2 in the ternary diagram; the substance is probably a solid solution. Precise determination of the composition of Mg petalite is complicated by metastable liquid separation taking place before crystallization, so that crystallization proceeds in separated liquid phases which have a composition different from that of the original homogeneous melt.

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KRYSTALIZACE TAVENIN A SKEL V SYSTÉMU $MgO — Al_2O_3 — SiO_2$ S NUKLEÁTORY $ZrO_2 + TiO_2$

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V literatuře věnované krystalizaci v systému $MgO—Al_2O_3—SiO_2$ je několik informací o metastabilní fázi Mg petalitu [2]—[5]. Mezi předpokládaným složením podle [2] a [5] jsou rozdíly (obr. 1), podobně jako v údajích o podmínkách jeho tvorby a přeměny na stabilnější fáze. Precipitaci Mg petalitu byla proto věnována hlavní pozornost.

Byla utavena skla, pro něž molární podíl $MgO/Al_2O_3 > 1$ (obr. 1). Pro docílení objemové krystalizace bylo použito nukleátorů 6 mol. % ZrO_2 + 3 mol. % TiO_2 stejné pro všechna složení. Skla s nižším obsahem Al_2O_3 byla opalescentní až bílá v následkem metastabilního odmísení během ochlazení taveniny na vzduchu (obr. 1).

Na základě údajů v [9], [11], [16] byla krystalizace prováděna přetavením primárního skla a rychlým ochlazením taveniny na krystalizační teplotu s výdrží po stanovenou dobu. Pro srovnání bylo použito i izotermní krystalizace skla.

Kromě složení 45 SiO_2, 15 Al_2O_3, 40 MgO (mol. % základních složek) všechny ostatní taveniny krystalovaly v objemu při vhodné krystalizační teplotě do 1000 °C. Výsledky práškové rtg. difrakční analýzy jsou na obr. 2.

Prvou krystalickou fází byla ZrO_2 — fáze (pravděpodobně tuhý roztok), experimentálně určené d a I/I_0 jsou v tab. I. Rentgenografické údaje pro Mg petalit jsou v tabulce II. Ze složení s obsahem 10 mol. % Al_2O_3 (sloupec A) se vylučoval Mg petalit, jehož d a I/I_0 byly poněkud odlišné od téže fáze krystalující ze složení s 15 mol. % Al_2O_3 (sloupec B tab. II).

Okruh složení poskytujících při krystalizaci Mg petalit je na obr. 3, kde je rozlišeno i množství této fáze u jednotlivých složení. Obsah další fáze — tuhé roztoky β — křemene, vzrůstal s posunem složení ke spojnici SiO_2 — spinel (tab. III).

Z výsledků v tabulce IV vyplývá, že krystalizace probíhá rychleji v tavenině než ve skle, rozdíly však byly i mezi sklem odmíseným a neodmíseným (připraveným drastickým ochlazením taveniny). Příčinou jsou pravděpodobně rozdíly v nukleaci, k níž dochází již v průběhu ochlazování taveniny [12], [16].

Podle výsledků v tabulce V a obr. 2, 4 dochází za vyšších teplot k rozpadu Mg petalitu a precipitaci tuhých roztoků β-křemene. Podmínky tvorby Mg petalitu při zahřívání skla byly sledovány DTA (obr. 5, 6).

Před krystalizací tavenin, které poskytovaly Mg petalit jako hlavní fázi, nastává odmísení. Podle výsledků na obr. 2 a podle [12] je zdrojem Mg petalitu i tuhých roztoků β-křemene (za vyšších teplot) odmísená fáze s vyšším obsahem SiO_2, z druhé nízkokřemičité fáze se vylučuje enstatit. Složení Mg petalitu je proto ve výše křemičité oblasti složení (cca 65—75 mol. % SiO_2) podobně jako uvádí Schreyer a Schairer [2] a pravděpodobně jde o tuhý roztok.

Obr. 1. Složení vyšetřovaných tavenin a skel v trojsložkovém diagramu v mol. %; ○ čirá skla, ⊗ opalescentní skla, ● zakalená skla, ◑ sklo rozdělené na dvě vrstvy; A — oblast metastabilního odmísení podle Varšala [6], B — oblast složení skel odměšujících při ochlazení podle Varšala [6].
Graficky rozlišené oblasti uvnitř diagramu jsou oblasti předpokládaného složení Mg petalitu podle [2] a [4].

Obr. 2. Průběh vylučování krystalických fází v závislosti na teplotě krystalizace tavenin a na jejich složení. Doba zpracování 30 min. Složení tavenin v mol. % SiO_2 /Al_2O_3/ MgO:
1 — 45/10/45 2 — 45/15/40 3 — 50/10/40
4 — 60/10/30 5 — 65/5/30 6 — 65/10/25
7 — 65/15/20 8 — 70/10/20 9 — 75/5/20 10 — 75/10/15
Δ ZrO_2 — fáze, ○ Mg petalit, ● enstatit, + tuhé roztoky β — křemene.

Obr. 3. Metastabilní oblast existence Mg petalitu; ○ složení poskytující při krystalizaci Mg petalit, × složení, u nichž nebyl Mg petalit zjištěn.

Obr. 4. Část záznamů z rtg. difrakční analýzy pro složení skla 65/15/20; 1 — krystalizace taveniny při 900 °C 30 minut, 2 — změna fázového složení po vystavení vzorku 1 teplotě 980 °C 90 minut, P — Mg petalit, Z — ZrO_2 — fáze, β — t. t. β — křemene.

Obr. 5. DTA, složení skla 65/10/25, rychlost vzestupu teploty 10 °C/min.

Obr. 6. DTA, složení skla 65/10/25, rychlost vzestupu teploty 2 °C/min.

КРИСТАЛЛИЗАЦИЯ РАСПЛАВОВ И СТЕКОЛ В СИСТЕМЕ $MgO—Al_2O_3—SiO_2$ С КАТАЛИЗАТОРАМИ КРИСТАЛЛИЗАЦИИ $ZrO_2 + TiO_2$

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В литературе по кристаллизации в системе $MgO—Al_2O_3—SiO_2$ приводятся некоторые данные относительно метастабильной фазы Mg петалита [2]—[5], но между предполагаемым составом согласно [2] и [4] имеются различия (рис. 1). Подобным образом расходятся данные о условиях его образования и превращения в более стабильную фазу. Поэтому в приводимой работе уделяется главное внимание кристаллизации Mg петалита.

Приготовили разные виды стекла с молярным отношением $MgO/Al_2O_3 > 1$ (рис. 1). Для получения объемной кристаллизации применяли катализаторы 6 мол. % ZrO_2 + + 3 мол. % TiO_2, одинаковые для всех составов. Стекла с более низким содержанием Al_2O_3 оказались опалесцентными с переходом в белый цвет в результате метастабильного расслоения во время охлаждения расплава на воздухе (рис. 1).

Согласно данным в [10], [14] проводили кристаллизацию путем переплавки первичного стекла, резко охлаждая расплав до температуры кристаллизации с установленной выдержкой. Для сопоставления пользовались тоже изотермической кристаллизацией стекла. Все расплавы, за исключением расплавов, содержащих 45 SiO_2, 15 Al_2O_3, 40 MgO (мол. % основных компонентов), кристаллизуют в объеме при подходящей температуре кристаллизации до 1000 °C. Результаты порошкового рентгеновского дифракционного анализа приводятся на рис. 2. Первой кристаллизующей фазой оказывается ZrO_2 — фаза (правдеподобно твердый раствор). Экспериментальным путем установленные фазы d и I/I- приводятся в табл. I. Рентгенографические данные относительно Mg петалита приведены в табл. II. Из состава, содержащего 10 мол. % Al_2O_3 (столб A) выделяется Mg петалит, d и I/I_0 несколько отличаются от той же фазы, кристаллизующей из состава, содержащего 15 мол. % Al_2O_3 (столб B в табл. II). Количество составов, дающих при кристаллизации Mg петалит, приводится на рис. 3, где различается даже количество той же фазы у отдельных составов. Содержание дальнейшей фазы — твердые растворы β-кварца, повышается в зависимости от смещения содержания к соединяющей прямой SiO_2 — шпинель (табл. III). При кристаллизации расплавов и стекол с низким содержанием SiO_2 выделялся энстатит как главная фаза. Из результатов, приводимых в табл. IV следует, что кристаллизация в расплаве протекает быстрее чем в стекле. Различия в скорости кристаллизации были также установлены между расслоенным и нерасслоенным стеклом (полученным резким охлаждением расплава). Правдеподобной причиной являются различия в нуклеации, протекающей уже во время охлаждения расплава [12], [16].

Согласно результатам в табл. V и на рис. 2, 4 при более высоких температурах происходит распад Mg петалита и кристаллизация твердых растворов β-кварца. Условия образования Mg петалита при нагревании стекла исследовались с помощью ДТА (рис. 5, 6).

До кристаллизации расплавов, дающих Mg петалит, которую считают основной фазой, проходит расслоение. Согласно результатам на рис. 2 о согласно [12] источником Mg петалита и твердых растворов β-кварца (при более высоких температурах) является расслоенная фаза с более высоким содержанием SiO_2, в то время как из фазы с низким содержанием кварца выделяется энстатит. Поэтому состав Mg петалита находится в области с более высоким содержанием кварца (приблизительно 65—75 мол. % SiO_2 и правдеподобно это твердый раствор).

Рис. 1. Состав исследуемых расплавов и стекол в трехкомпонентной диаграмме в мол. %; ○ *— прозрачные стекла,* ⊕ *— опалесцентные стекла,* ● *— глушеные стекла,* ◑ *— стекло, разделенное на два слоя; A — область метастабильного расслоения согласно Варшаву* [6], *B — область состава стекол, у которых при охлаждении согласно Варшаму* [6] *проходит расслоение. Графически отличающиеся области внутри диаграммы представляют собой области предполагаемого состава* Mg *петалита согласно литературе* [2] *и* [4].

Рис. 2. Ход выделения кристаллических фаз в зависимости от температуры кристаллизации расплавов. Время термообработки 30 мин. Состав расплавов в мол. % $SiO_2/Al_2O_3/MgO$:

1 — 45/10/45 *2 — 45/15/40* *3 — 50/10/40*
4 — 60/10/30 *5 — 65/5/30* *6 — 65/10/25*
7 — 65/15/20 *8 — 70/10/20* *9 — 75/5/20*
10 — 75/10/15

△ — ZrO_2-фаза, ○ — Mg *петалит*, ● — *энстатит*, + — *твердые растворы* β-*кварца.*

Рис. 3. Метастабильная область существования Mg *петалита:* ○ — состав, *дающий при кристаллизации* Mg *петалит*, × — *состав, у которого* Mg *петалит не был установлен.*

Рис. 4. Рентгенограммы для состава 65/15/20; 1 — кристаллизация расплава при температуре 900 °C, время 30 мин., 2 — изменение состава фаз пробы 1, подвергаемой температуре 980 °C во время 90 мин., P — Mg *петалит,* **Z** — ZrO_2-*фаза,* β — *твердый раствор* β-*кварца.*

Рис. 5. ДТА, состав стекла 65/10/25, скорость подъема температуры 10 °C/мин.

Рис. 6. ДТА, состав стекла 65/10/25, скорость подъема температуры 2 °C/мин.