Method of mathematical modelling of experiments as a manner for investigation of composition-property correlation of high-siliceous part of the Al_2O_3-B_2O_3-SiO_2 glass system

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The investigations of interrelations between composition and property of glasses are prevailing for understanding of the glass-formation regularity, nature and structural speciallity of the glassy state. The problem is not so difficult, when glass-forming occurs at the comparatively low temperatures (1400-1500^{0}C), allowing to prepare research samples relatively easy. The investigation of refractory glass-forming systems, when the glass-forming occurs at the temperature over 1550-1600^{0}C is quite different task. For example glass-forming basis of so-called 'graded glasses' is just the same. They correspond to high-siliceous part of Al_2O_3-B_2O_3-SiO_2 system, where the SiO_2 percentage is into 80-97 mass %. The analysis of our investigations demonstrated, that even with the help of limited quantity of points existing on the composition-properties diagram and using mathematical methods of planning of experiment is possible to represent all glass characteristics. In this work we tried to calculate LETC, density, viscosity and electrical conduction of Al_2O_3-B_2O_3-SiO_2 glass system in the range where the percentage of Al_2O_3 is 0-20 mass %, B_2O_3 is 0-20 mass % and SiO2 80-100 mass % by the method of Sheffe simplex latticed planes. Results of accounts demonstrate good correlation between calculated and experimental data.

In order to understand regularity of glass-forming, structure features, physical-chemical behavior of glasses the research of composition-property correlation is used very widely. The problem is not so difficult, when glass-forming occurs at comparatively low temperatures (1400 - 1500^{o}C). This temperature range is more or less available for preparation of the samples, which can be tested by direct methods of physical-chemical analysis. The investigation of glass-forming, when this process occurs at the temperature over 1550-1600^{o}C, is quite different task. For example, glass-forming basis of so-called "graded glasses" is just like that. They correspond to high-siliceous part of Al_2O_3-B_2O_3-SiO_2 system, where the SiO_2 percentage is into 80-97 mass %. The analysis of our investigations demonstrate, that using limited quantity of the experimental points, located on the composition-properties diagram, it is possible to represent the all glass characteristics with help of mathematical methods of planning of the experiment. In this work using the method of Sheffe simplex latticed planes we tried to calculate LETC, density, viscosity and electrical conduction of the Al_2O_3-B_2O_3-SiO_2 glass system in the range where the percentage of Al_2O_3 is 0-20 mass%, B_2O_3 is 0-20 mass % and SiO_2 is 80-100 mass %. In this connexion it is necessary to notice the following circumstances:

1. Dependence of above-marked properties on composition is rather complicated and can not be described by the low power polynomial;

2. At measurement of viscosity composition of many selected by us triangle glasses - (SiO_2 – 80% + Al_2O_3 –20%)--(SiO_2,-80% + B_2O_3-20%)] -SiO_2 were crystallized. Therefore the data of these glasses for simplex latticed plane were obtained by extrapolation of corresponding graphical construction. Besides, in case of the values of responses were obtained by graphical method, the experimental data were used as an additional data for testing of adequacy of obtained formulas.

The calculations showed that the formulas for the properties of the above–mentioned glasses, obtained by cubic polynomial, do not provide a required precision. There are two possibilities for increasing of the accuracy: either complication of the polynomial or narrowing of region of the glass compounds. We choose the second one, as the most efficient. For example, for several glass compounds we narrowed the region up to [(SiO_2-88%+Al_2O_3-12%)-(SiO_2-88% + B_2O_3-12%)] – SiO_2.

Thus the formula of LETC into 20-300^{0}C is presented as:

$$\alpha_{20\text{-}300} \times 10^{-7} = 17.5X_1+6.4X_2+9.0X_3+2.025X_1X_2-18.0X_1X_3+6.075X_1X_2(X_1-X_2)-15.66X_1X_3(X_1-X_3)+0.473X_2X_3(X_2-X_3)-45.5X_1X_2X_3 \quad (1)$$

As is obvious, this is the cubic polynomial and it is correct for the triangle: (SiO_2-88%+B_2O_3-12%)-SiO_2-(SiO_2-88%+Al_2O_3-12%). In formula (1) X_1=B_2O_3/12, X_3= Al_2O_3/12, and X_2= (1-Z/12), where Z is sum of percent by weights of B_2O_3 and Al_2O_3 or Z = 100-[SiO_2]. The oxides, presented in brackets are the corresponding oxides in mass%. The results of testing of the mathematical model adequacy for the examined glasses to the LETC dependence are presented in Table 1.

Table 1

Glass N°	X_1	X_2	X_3	$\alpha_{exp.}$x10^{-7}	$\alpha_{calc.}$ x10^{-7}	$\lvert\Delta\alpha\rvert$	ξ	T_{exp}
2	0.229	0.771	0	9.2	8.7	0.5	0.9	2.04
4	0.917	0.083	0	17.1	17.1	0	0.9	0
6	0	0.771	0.229	7.3	7.04	0.26	0.9	1.06
8	0	0.083	0.917	9	8.75	0.25	0.9	1.02
15	0.458	0.084	0.458	8.3	8.97	0.67	0.8	2.74
16	0.229	0.542	0.229	6.7	6.1	0.6	0.8	2.65

Reproducibility of the measurements is ±1.0x$10^{-7}$$K^{-1}$. When the number of parallel experiments is n=2 and reproducibility dispersion is S^2_y=0.25, the value of Students criterion, calculated by formula

$$t = \Delta\alpha\sqrt{n} / S_y^2\sqrt{1+\xi} \quad (2)$$

is equal to 4.1. It can be seen from Table 1, that experimental values of $t_{exp.}$ are smaller than this value. It confirms an adequacy of the mathematical model. These data show that the dependence of density on the SiO_2 is complicated if the weight correlation of B_2O_3 and

Al_2O_3 is equal to 1:1. Because of this (as in case of LETC) the simplex was contracted up to 88% of SiO_2 content. The following equation was obtained:

$$d_{20}=2.125X_1+2.397X_2+2.317X_3-0.3195X_1X_2+0.0135X_1X_3-0.56X_2X_3-0.007425X_1X_2(X_1-X_2)+0.189X_2-X_3(X_2-X_3)+2.73X_1X_2X_3 \quad (3)$$

In Table 2 comparison of the experimental and calculated data on density are presented. The value of X_1, X_2, X_3 is determined like before.

Table 2

Glass N°	X_1	X_2	X_3	$d_{20\ exp.}$	$D_{calc.}$	$\|\Delta d\|$	$T_{exp.}$
16	0.229	0.542	0.229	2.2121	2.281	0.069	2.42
2	0.229	0.771	0	2.2941	2.271	0.023	0.8
4	0.9167	0.0833	0	2.1359	2.128	0.008	0.27
7	0	0.542	0.458	2.175	2.221	0.056	1.95
8	0	0.0833	0.9167	2.285	2.27	0.015	0.52

It can be seen from the Table 2, $t_{exp.}$ is always smaller than tabular one, which is ~5.0 by formula (2) when n=2, S^2_y=0.015 and $|\Delta d|$=0.07- this correspond to probability ~ 90%.

The equation for temperature of 1500^{0}C was derived for the electro-conductivity and for viscosity. At 1500^{0}C -

$$-\lg\chi_{1500}=4.22X_1+3.83X_2+3.68X_3+1.35X_1X_2-1.553X_1X_3-0.9675X_2X_3-0.54X_1X_2(X_1-X_2)-1.553X_1X_3-0.9675X_2X_3-0.54X_1X_2(X_1-X_2)-0.27X_1X_3(X_1-X_3)-0.7425X_2X_3(X_2-X_3)-7.022X_1X_2X_3 \quad (4)$$

Results of the testing of equation (4) suitability are presented in Table 3. It is correctly for broad region of compositions than equations for LETC [equation (1)] and density [equation (3)]. It covers triangle (SiO_2-80%+Al_2O_3-20%)-SiO_2-(SiO_2-80%+B_2O_3-20%). At that, X_1, X_2, and X_3 is possible to determine by formulas:

$$X_1=[B_2O_3]\ 5/100,\quad X_2=[Al_2O_3]\ 5/100,\quad X_3=[100-5([Al_2O_3]+[B_2O_3])]/100 \quad (5)$$

Table 3

Glass N°	X_1	X_2	X_3	$-\lg\chi_{exp}$	$-\lg\chi_{calc.}$	$\|\Delta\lg\chi\|$	t_{exp}
2	0.1375	0.8625	0	4.02	4.10	0.08	5.6
8	0	0.45	0.55	3.52	3.50	0.02	1.2
12	0.275	0	0.725	3.54	3.52	0.02	1.2
13	0.55	0.175	0.275	3.61	3.64	0.03	1.55
15	0.275	0.45	0.275	3.54	3.58	0.04	2.1

The tabular value t_T is estimated as ~7.0 at n=2, S^2_y=0.002. It can be seen from the Table 3, all $t_{exp.}$ values are smaller than this limit. It means that the probability of determination of the -lgχ with accuracy ±0,15 is more than 90%.

The complicated dependence of viscosity on the investigated glass compositions causes the narrowing of the triangle up to $\Sigma[R_2O_3]$=12%, i.e. (as in the case of LETC and density) it is need to use (SiO_2-88%+B_2O_3-12%)-SiO_2-(SiO_2-88%+Al_2O_3-12%) triangle and the cubic polynomial. The following formula is obtained for 1500°C:

$$\lg\eta_{1500}=6.74X_1+8.94X_2+7.95X_3-1.4175X_1X_2-1.755X_1X_3-0.567X_1X_2(X_1-X_2)-0.365X_1X_3(X_1-X_3)+2.835X_2X_3(X_2-X_3)-4.455X_1X_2X_3 \quad (6)$$

The results of the testing of this formula adequacy presented in Table 4. The table shows that $t_{exp.}$ is always smaller than tabular one, which is equal to ~5.4 at $\Delta\lg\eta$=0.25, n=2 and S^2_y=0.05 . It means that lgη can be calculated by the formula (6) with probability ~ 90%.

Table 4

Glass N°	X_1	X_2	X_3	$Lg\eta_{exp}$	$Lg\eta_{calc.}$	$\|\Delta\lg\eta\|$	T_{exp}
2	0.25	0.75	0	5.28	5.3	0.02	0.43
6	0	0.75	O.25	6.45	6.2	0.25	7.05
15	0.5	0	0.5	4.96	4.96	0.02	0.43
16	0.25	0.5	0.25	5.22	5.52	0.3	8.46

Thus, the mathematical models of dependence of the LETC, density, electro-conductivity and viscosity on high-siliceous glasses compounds (formulas (1), (3), (4) and (6)) permit to calculate the value of these properties with tolerable for practice precision.

Current high-siliceous glass viscosity values of the Al_2O_3-B_2O_3-SiO_2 system permit to develop formula for calculation of temperature of start of the deformation – T_{sd}.

It is known well, that this temperature is between temperatures corresponding to viscosity of 10^{11}-10^{12} poise. Taking T_{sd} as the temperature at which the viscosity of our glasses is $10^{11.5}$ poise, and defining this temperature by well-known equation of simple exponent for each glass prototype, it is possible to derive equation for calculation of T_{sd}:

$$T_{sd}=1025X_1+1362X_2+1220X_3-83.25X_1X_2-546.75X_1X_3-49.5X_2X_3+83.025X_1X_2(X_1-X_2)+249.5X_1X_3(X_1-X_3)-18.225X_2X_3(X_2-X_3)-2478.6X_1X_2X_3 \quad (7)$$

Equation (7) is right for $SiO_2\geq89\%$ and $\sum(Al_2O_3+B_2O_3)\leq11\%$ glasses. The comparison of calculated and experimental values of T_{sd} for some glasses are presented in Table 5.

Table 5

Glass	15	16	3	7
T_{sd} (calc) °C	977	1090	1180	1280
T_{sd}(calc)°C	985.7	1110	1172	1278
ΔT_{sd} °C	8.7	20	8	2
$T_{exper.}$	2.02	4.65	1.86	0.47

At calculation of T_{sd} with accuracy ±25°C, S^2_y =4.3 and n=2 tabular value T_{sd} is 5.8, what corresponds to 90% probability. Presented in Table 5 data show that t_{exp} for the control glasses are always smaller than tabular values, what confirms the adequacy of derived equation (7).

Thus, summarizing the obtained results, we can establish that the used model of experiment planning by the method of Sheffe permits to calculate and to obtain with 90% probability and with minimal quantity of experimental points the composition-properties correlation for the glasses of high-siliceous part of Al_2O_3-B_2O_3-SiO_2 system.