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CALCULATION OF OPTICAL CONSTANTS OF GLASSES IN THE $PbO-B_2O_3-SiO_2-GeO_2$ OXIDE SYSTEM

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The lead silicate system underlies many compositions of optical glasses with a high refractive index. Such expensive and rare earth oxides as GeO_2, La_2O_3, Ga_2O_3, Bi_2O_3, etc. are also introduced into the composition of these glasses, besides the conventional oxides. The development of new compositions of optical glasses is most frequently carried out by a pilot and experimental method being a labor-intensive process and requiring the considerable material expenses for performing the experimental research. It is possible to appreciably decrease the scope of experiments using the calculation methods of preliminary estimation of the glasses properties. The purpose of this work was to develop the mathematical models of calculation for $PbO-B_2O_3-SiO_2-GeO_2$ based glasses, depending on their composition and optical constants (refractive index n_D, mean dispersion (n_F-n_C) and dispersion coefficient ν_D). In order to establish the interrelation between the optical constants and the composition of multicomponent oxide glasses, the development of mathematical models was carried out using an experimentally statistical method. The developed mathematical models are adequate to the experimental data and allow calculating the optical constants of glasses with the following mean-square deviations: $n_D=\pm0.014$, $(n_F-n_C)=\pm11.1\cdot10^{-4}$, and $\nu_D=\pm0.4$. The specified accuracy is sufficient for solution of different practical tasks, which are connected with the selection of compositions of the optical glasses with a preset complex of the optical properties.

Keywords: oxide glasses, optical glass, refractive index, dispersion coefficient, mathematical modeling, additive coefficients.

Introduction

The $PbO-SiO_2$ oxide system is the base of chemical compositions of many optical glasses [1]. The PbO content in known compositions of glasses varies widely from 10 to 70 mol.%. Besides the base components, the compositions of specified glasses contain also K_2O, Na_2O, B_2O_3, BaO, TiO_2 and other oxides in small quantities.

When developing new glasses which are notable for the special optical properties, the scarce and expensive oxides GeO_2, La_2O_3, Ga_2O_3, Bi_2O_3, TeO_2, CdO, etc. are also introduced into their compositions, besides the conventional components.

As a rule, new compositions of glasses with the preset values of optical constants, such as the refractive index n_D, the mean dispersion (n_F-n_C), and the dispersion coefficient $\nu_D=(n_D-1)/(n_F-n_C)$ are created on a pilot experimental basis. This method requires the considerable material expenses, which may be reduced using the calculation methods for a preliminary estimation of indicated properties. However, for the optical glasses, which compositions along with PbO may contain considerable amounts of GeO_2, La_2O_3, Ga_2O_3, Bi_2O_3, TeO_2, CdO and other oxides, the known methods for calculation of n_D, (n_F-n_C) and ν_D are inapplicable [1,2].

Therefore, the purpose of this work was to develop the mathematical models of calculation for the $PbO-B_2O_3-SiO_2-GeO_2$ multicomponent glasses, depending on their composition and optical constants (n_D, (n_F-n_C) and ν_D).

Calculations

The development of the mathematical models was carried out by the method of multiple correlations [3]. The regression equation of the following form was used to describe the dependence between the properties and compositions of the multicomponent glasses:

$$\hat{y} = \sum_{i=1}^{n} b_i x_i \ , \qquad (1)$$

where $\hat{y}$ is the calculation value of glass properties; b_i are the regression coefficients; x_i is the content of components in the glass, mol.%.

The values of regression coefficients were estimated by the least square method [4] based on three experimental samples of the glass compositions with the known values of optical constants n_D, (n_F-n_C) and ν_D, which were drawn with the use of the SciGlass electronic database [5].

The approximation accuracy of the experimental values of optical constants by a regression equation (1) was estimated by comparison of the residual dispersions S^2_{res} with the dispersions relative to the mean values of S^2_y. The specified dispersions were calculated according to the following formulae:

$$F = \frac{S^2_y}{S^2_{res}},\ S^2_y = \frac{\sum_{i=1}^{n}(y_i - \overline{y})^2}{n-1},$$

$$\overline{y} = \frac{\sum_{i=1}^{n} y_i}{n},\ S^2_{res} = \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n-\ell}, \quad (2)$$

Table 1

Numerical characteristics of experimental samples

No.	Optical constants	Amount of sample, n	Range of values of optical constants	Sample mean, $\overline{y}_i$	Mean-square deviation, S_y
1	Refractive index, n_D	861	1.540–2.249	1.848	0.126
2	Mean dispersion, (n_F-n_C)	375	$(130–636)\cdot10^{-4}$	$334\cdot10^{-4}$	$97\cdot10^{-4}$
3	Dispersion coefficient, ν_D	394	14–46	25.61	5.88

Table 2

Regression coefficients and their mean-square deviations for calculation of the optical constants of glasses according to Eq. (1)

No.	Oxide	Refractive index, $n_i\cdot10^2$	Mean dispersion, $\Delta n_i\cdot10^3$	Dispersion coefficient, $\nu_i\cdot10^2$	Limits of component content, mol.%
1	Al_2O_3	1.514±0.019	3321±306	61.6±1.1	0–20
2	B_2O_3	1.411±0.004	–1623±84	50.2±0.3	0–60
3	BaO	1.857±0.035	4724±322	52.8±1.3	0–20
4	Bi_2O_3	3.165±0.064	22006±2134	–40.1±7.6	0–10 (5*)
5	CdO	2.105±0.040	4656±500	14.4±1.9	0–20
6	Ga_2O_3	1.631±0.025	1735±336	36.1±1.4	0–20
7	GeO_2	1.665±0.004	1095±78	35.1±0.3	0–70
8	K_2O	1.285±0.035	–1879±732	59.4±2.9	0–10
9	La_2O_3	2.525±0.068	2552±762	26.5±3.1	0–12
10	Li_2O	1.853±0.063	5069±755	23.3±3.3	0–10
11	Na_2O	1.607±0.032	1436±483	24.7±2.0	0–10
12	PbO	2.365±0.003	9507±66	0.7±0.2	10–85 (70*)
13	SiO_2	1.437±0.003	–1174±60	42.3±0.2	0–60
14	SrO	1.872±0.212	4672±917	30.9±6.9	0–6
15	TeO_2	1.901±0.048	6413±852	15.9±3.4	0–10
16	TiO_2	2.389±0.037	11484±543	–11.4±2.2	0–10
17	ZnO	1.941±0.017	3246±227	30.8±1.0	0–20
18	ZrO_2	2.243±0.072	5270±821	32.6±3.9	0–9

Note: * – The limits of component content for calculation of (n_F-n_C) and ν_D.

where F is the calculation value of Fisher's criterion; S_y^2 is the sampling variance of the values of properties; S_{res}^2 is the residual variance; $\overline{y}$ is the sample mean of property; y_i is the experimental value of the i-th glass property; $\hat{y}_i$ is the calculation value of the i-th glass property; n is the size of the experimental sample; and ℓ is the number of coefficients in the regression equation (equaling to 18, which is the number of components).

The more the value of S_y^2 exceeds the value of S_{res}^2, the more accurately the regression equation approximates the experimental data.

Results and discussion

The results of the statistical analysis of the initial experimental samples and the limits of component content in the glasses are listed in Tables 1 and 2.

It is necessary to point out that the glasses being included in the experimental samples are distinguished by the mean values of refractive index (n_D=1.848±0.12) combined with the low values of dispersion coefficient (ν_D=25.6±5.9). The optical glasses with such combination of n_D and ν_D can be qualified as the dense flint glasses (TF), extra dense flint glasses (CTF) or heavy barium flints (TBF) according to the Abbe diagram [6].

The values of the regression coefficients in the equations (1) for the calculation of the optical constants of glasses, depending on their composition, are listed in Table 2. It follows from the data presented in Table 3 that the developed equations adequately describe the experimental data and allow calculating the optical constants n_D, (n_F-n_C) and ν_D for glasses with the indicated limits of component content with a sufficiently high accuracy. The stated facts are also confirmed by the results of calculation of the optical constants for the single practical compositions of lead-containing glasses (Table 4). It is possible to increase the accuracy of the calculation of the optical constants of glasses due to an increase of the extent of approximating equation.

Taking into account the fact that the regression coefficients in Eq. (1) are the estimations of the partial contributions of oxides to the glass properties [3,4], the analysis of their values can be performed on the basis of the selection of the most preferable components and their quantitative content in the compositions of above-mentioned flint glasses with a preset complex of optical constants and other properties.

It follows from the graph shown in Figure 1 that the glass-forming oxides are arranged according to the extent of increase of the refractive index of lead-containing glasses in the following sequence: $B_2O_3<SiO_2<GeO_2$. The oxides of the following series: $CdO<ZrO_2<PbO<TiO_2<La_2O_3<Bi_2O_3$ are qualified as the components of glasses being promoted an increase in their refractive index to the fullest extent.

Taking into consideration the correlation dependence shown in Figure 2, the specified

Table 3

Results of statistical analysis of the regression equations

No.	Name of optical constants	Sample variance, S_y^2	Residual variance, S_{res}^2	Fisher's criterion, F	Mean deviation, $\hat{y}_i - y_i$
1	Refractive index, n_D	0.01575	0.00031	50.8	±0.014
2	Mean dispersion, (n_F–n_C)	$9409\cdot10^{-4}$	$207\cdot10^{-4}$	45.5	$\pm11.1\cdot10^{-4}$
3	Dispersion coefficient, ν_D	34.57	0.336	102.9	±0.4

Table 4

Chemical compositions of glasses and values of their optical properties

No.	Content of components, mol %							Experimental values			Calculation values		
	PbO	B_2O_3	SiO_2	GeO_2	Ga_2O_3	La_2O_3	Al_2O_3	n_D	(n_F–n_C)	ν_D	n_D	(n_F–n_C)	ν_D
1	68.2	31.8	0.0	0.0	0.0	0.0	0.0	2.063	636.0	16.70	2.061	597.0	16.40
2	65.0	12.1	19.6	0.0	0.0	0.0	3.3	2.044	619.4	16.86	2.040	586.3	16.84
3	42.4	22.6	0.0	30.1	0.0	4.8	0.0	1.947	411.7	23.00	1.946	411.5	23.50
4	50.3	0.0	49.7	0.0	0.0	0.0	0.0	1.906	419.4	21.60	1.904	419.9	21.40
5	46.9	11.9	41.2	0.0	0.0	0.0	0.0	1.871	364.4	23.90	1.869	378.0	23.70
6	20.0	0.0	0.0	70.0	10.0	0.0	0.0	1.801	281.2	28.50	1.802	284.1	28.30
7	40.1	5.4	54.5	0.0	0.0	0.0	0.0	1.798	302.2	26.40	1.807	308.5	26.10

components in lead-containing glasses also promote an increase of the mean dispersion and a decrease of the dispersion coefficient.

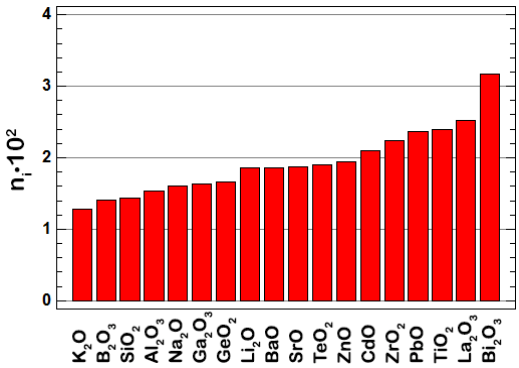

Fig. 1. Sequence of the arrangement of oxides according to the amount of their contribution to the values of glass refractive index

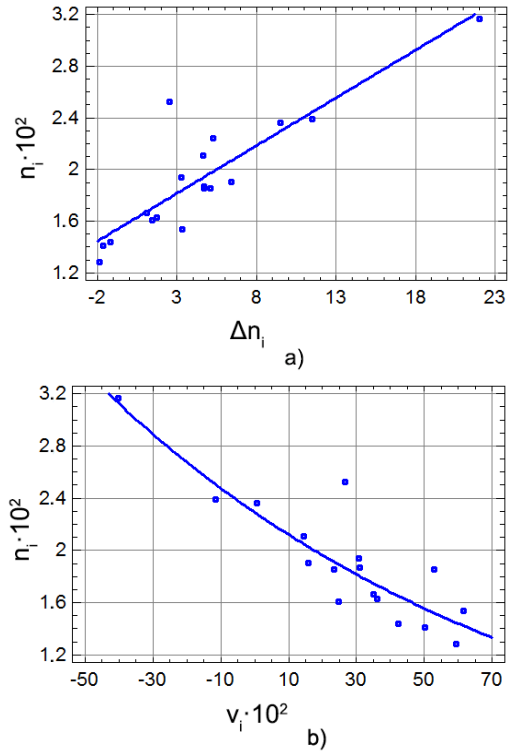

Fig. 2. Correlation between the partial contributions of oxides to the values of refractive index and mean dispersion (a), refractive index and dispersion coefficient (b)

Thus, it can be concluded that the $PbO–SiO_2–GeO_2$ oxide system can be used as a base of new compositions of glasses, which are distinguished by higher values of refractive index combined with the low value of dispersion coefficient. Additionally, these glasses can also contain TeO_2, ZnO, CdO, Bi_2O_3, La_2O_3, TiO_2 and ZrO_2 in small amounts.

Conclusions

We developed the mathematical models which adequately describe the experimental data and allow calculating the optical constants n_D, $(n_F–n_C)$ and ν_D with a sufficiently high accuracy. These models can be used when developing the new compositions of optical glasses, in particularly for the multicomponent glasses based on the oxide system $PbO–B_2O_3–SiO_2–GeO_2$.

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РОЗРАХУНОК ОПТИЧНИХ ПОСТІЙНИХ СТЕКОЛ В ОКСИДНІЙ СИСТЕМІ $PbO-B_2O_3-SiO_2-GeO_2$

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Свинцевосилікатна система лежить в основі багатьох складів оптичних стекол з високим показником заломлення. Крім традиційних оксидів до складу цих стекол також вводять високовартісні й рідкоземельні оксиди такі, як: GeO_2, La_2O_3, Ga_2O_3, Bi_2O_3 та інші. Розробку нових складів оптичних стекол найчастіше проводять дослідно-експериментальним шляхом, що є трудомістким процесом і вимагає значних матеріальних затрат на проведення експериментальних досліджень. Суттєво зменшити обсяг експериментів можна за рахунок використання розрахункових методів попереднього оцінювання властивостей стекол. Метою цієї роботи було для стекол в базовій оксидній системі $PbO-B_2O_3-SiO_2-GeO_2$ розробити математичні моделі для розрахунку в залежності від їх складу оптичних постійних, таких як: показник заломлення n_D, середня дисперсія (n_F-n_C) та коефіцієнт дисперсії ν_D. Розробку математичних моделей для встановлення взаємозв'язку оптичних постійних від складу багатокомпонентних оксидних стекол виконано експериментально-статистичним методом. Отримані математичні моделі адекватні експериментальним даним і дозволяють розраховувати оптичні постійні стекол зі середньоквадратичними відхиленнями $n_D=\pm0{,}014$, $(n_F-n_C)=\pm11{,}1\cdot10^{-4}$, $\nu_D=\pm0{,}4$. Зазначена точність є достатньою для вирішення різних практичних завдань, які пов'язані з вибором складів оптичних стекол з заданим комплексом оптичних властивостей.

Ключові слова: оксидні стекла, оптичне скло, показник заломлення, коефіцієнт дисперсії, математичне моделювання, адитивні коефіцієнти.

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