

X-ray Fluorescence Analysis of Lithium Borate Glass $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3 : \text{M}_x\text{O}_y$ (M = Al, Si, Ti, V, Mn, Fe)

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Abstract—X-ray fluorescence of lithium borate glass with various additives is studied. The possibility of the mutual influence of glass components, as well as equipment, on the results of X-ray analysis is shown. The conditions under which this method can be used for analytical purposes are formulated.

Keywords: borate glass, X-ray fluorescence, graduation

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INTRODUCTION

One of the major problems in the synthesis of glass is determining its precise chemical composition, as the composition determines the structure and properties of glass. In contrast to the synthesis of crystalline solids, in which the strict stoichiometric ratios between the components are valid, in the synthesis of glass, uncontrollable changes in the composition can take place due to the evaporation of certain volatile components of the glass melt, the interaction of the melt with the container material and gaseous atmosphere, and the phase separation of the melt as a result of liquation or nucleation of the crystalline phase.

Traditional chemical analysis of the composition of glass is a time-consuming and complicated process and can be accomplished, especially in the case of multi-component glass, only by a highly qualified team of analytical chemists; therefore, it is most often assumed that the composition of glass corresponds to the composition of a batch, i.e., mixtures of starting components, which a priori introduces an error in determining the composition.

As an alternative method for determining the composition of glass, X-ray fluorescence analysis can be used, based on the dependence of the intensity of characteristic (fluorescent) x-ray emission of the components of the substance on their concentration. However, to perform the analysis, pregrading is necessary—obtaining the dependence of the intensity of X-ray fluorescent radiation of the analysis element on its concentration in the sample. This relationship can be found experimentally or theoretically by calculating the flow density of the X-ray fluorescence radiation.

For instance, for small concentrations of analysis element A , it can be calculated by equation [1]:

$$n_i^A = k_i n_1 \tau_{m1}^A \frac{C_A}{\alpha} \left[1 - \frac{1 - \exp(-\alpha \rho d)}{\alpha \rho d} \right].$$

Here $k_i = \frac{\Omega}{4\pi} s_0 r_K^A \omega_K^A p_{Ki}^A$; Ω is the detector of the aperture or crystal-analyzer; s_0 is the area of the irradiated surface of the sample; r_K^A is a fraction of the radiation of the X-ray tube (primary radiation) absorbed at the K level of element A ; ω_K^A is the fluorescence yield of the K level of element A ; p_{Ki}^A is the probability of emission of the i th line of the K series of element A ; n_1 is the flow density of primary radiation; τ_{m1}^A is the mass absorption coefficient of the primary radiation in the pure element A ; C_A is the mass fraction of analysis element A ; $\alpha = \frac{\mu_{m1}}{\sin \varphi} + \frac{\mu_{mi}}{\sin \psi}$; μ_{m1} is the mass attenuation coefficient of the primary radiation by sample; μ_{mi} is the mass attenuation coefficient of the fluorescence radiation of the analysis element (secondary radiation) by the sample; φ is the incident angle of the primary radiation on the sample; ψ is the exit angle of the secondary radiation from the sample; ρ is density of the sample; and d is the thickness of the emitting layer.

This relationship implies, in particular, that in the cases when the attenuation coefficients vary slightly with a change in the composition, the dependence of the fluorescence emission of the analysis element on its mass fraction will be linear, since all other quantities are constant. In the general case, deviations from

linearity both in the positive and in the negative direction are possible.

The above equation does not take into account, however, the mutual influence of the components, at which fluorescence emission of the analyte can be excited not only by primary radiation but also the secondary radiation of the heavier element. In this case, the intensity of the light element will be overstated, and the intensity of the heavier element will be understated. Furthermore, this equation and similar equations for other types of samples do not take into account the effect of radiation scattering both in the sample and apparatus details. Appropriate adjustments may be calculated theoretically [1, 2]; however, in many cases, the calibration characteristics are easier to obtain experimentally. In this case, at the first stage, the intensity of the X-ray fluorescence radiation of the components of the comparison samples, whose composition is known with a high degree of accuracy, is measured. Further, calibration characteristics are obtained in the form of regression equations or graphs of the intensity on the component concentrations. Then, the resulting calibration characteristics are used to determine the concentration of the components of the studied materials according to their intensity.

This technique has been proposed, in particular, for determining arsenic, sulfur, germanium, and selenium in chalcogenide glass [3–8], as well as to determine the composition of rocks fused with lithium borate glass [9]. These studies for oxide glass, in particular, borate and borosilicate, are not known for us.

The purpose of the paper is to investigate the possibility of using X-ray fluorescence analysis to determine the composition of borate and borosilicate glass.

EXPERIMENTAL

To accomplish this task, either SiO_2 (2.9 and 5.5 wt %), Fe_2O_3 (0.15 and 0.30 wt %), vanadium oxides V_2O_3 , VO_2 , and V_2O_5 (0.4, 2, 4 wt %), or a mixture of oxides in the form of the standard sample of chamotte soK2g (4.8 and 9.1 wt %) were introduced into the glass. Pure oxides, the standard chamotte sample soK2g [10] (58.6 SiO_2 , 35.1 Al_2O_3 , 0.40 CaO , 0.48 MgO , 2.94 Fe_2O_3 , 0.060 MnO , 1.91 TiO_2 , 0.19 Na_2O , 0.69 K_2O wt %), lithium carbonate (Li_2CO_3), and boric acid (H_3BO_3) were used as raw ingredients. All the reagents are reagent-grade.

Before cooking the glass, a batch, pulverized and thoroughly mixed in porcelain mortar, was poured into an alundum crucible which was placed in an oven. The temperature of the oven was raised in steps from ambient to 250°C for 2.5–3 hours to remove the adsorbed moisture and decomposition of boric acid. Further, the crucibles were transferred to a muffle oven, preheated to 250°C, in which the temperature was also increased stepwise to 1000°C for 2 h to decompose the main mass of lithium carbonate. The

resulting melt was kept at this temperature for an additional 1 h, and then was poured into a graphite mold and heated to 530°C. The mold with the sample was placed in a muffle furnace, also heated to 530°C for annealing. After annealing for 30 minutes, the oven was turned off and the sample in the oven was cooled slowly to room temperature for 24 hours.

The annealing quality was checked on a PKS-250 polariscope-polarimeter by the absence of interference bands. After grinding and polishing the annealed glass, the samples for study were clear discs with a diameter of 40 mm and thickness of 4 mm and 8 mm. In some cases, only one side was ground and polished. For each chemical composition, from two to four samples were prepared.

The resulting samples were studied on the X-ray spectrometer SRM-25 with the X-ray optical circuit scheme of the spectrometric channels by Johann and Johannsen. X-ray tube 3RKhV2 with a positive voltage polarity on the anode was used; the anode material is Rh. As an X-ray detector, a flow proportional counter was used. The tube voltage was 40 kV, the current was 30 mA, and the exposure time was 40 s. Upon irradiation of the samples, K_α -radiation of Al, Si, Ti, V, Mn, and Fe was simultaneously recorded. To determine the background radiation of these elements, samples of pure lithium-borate glass $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ were used. Each sample was studied at least thrice, and then the data on the intensity were averaged. Furthermore, the data were averaged also for different samples of the same composition. The weighted average of the intensity of each element was determined by formula [11]:

$$\hat{I} = \frac{\sum_{i=1}^n \omega_i \bar{I}_i}{\sum_{i=1}^n \omega_i}$$

In this equation \bar{I}_i is the average intensity value obtained on the i th sample; $\omega_i = \frac{1}{\sigma_i^2}$ – is the statistical weight of the average intensity value obtained on the i th sample; σ_i is the mean square measurement error of the intensity on the i th sample; $\sigma_\omega = \sqrt{\frac{1}{\sum_{i=1}^n \omega_i}}$ is the mean square deviation of the weighted average assessment of the intensity; $\varepsilon = u_{(1+\gamma)/2} \sigma_\omega$ is the absolute accuracy of the weighted average of the estimated intensity; and $u_{(1+\gamma)/2}$ is the quantile of the normal distribution chosen for the confidence level of 0.95.

RESULTS

The intensity of the K_α -radiation of the element introduced into the composition of the lithium-borate

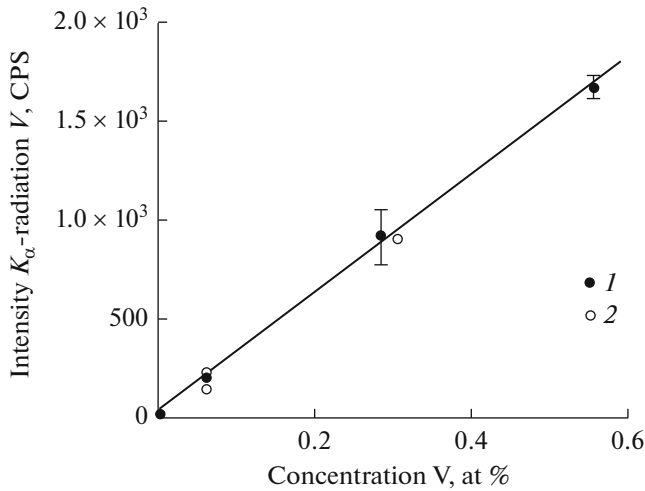


Fig. 1. Dependence of the K_{α} -radiation intensity of V on the atomic fraction of vanadium in $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass in the form of V_2O_5 oxide (1) or in the form of V_2O_3 or VO_2 oxides (2); the solid line is the calibration graph constructed according to the data for V_2O_5 .

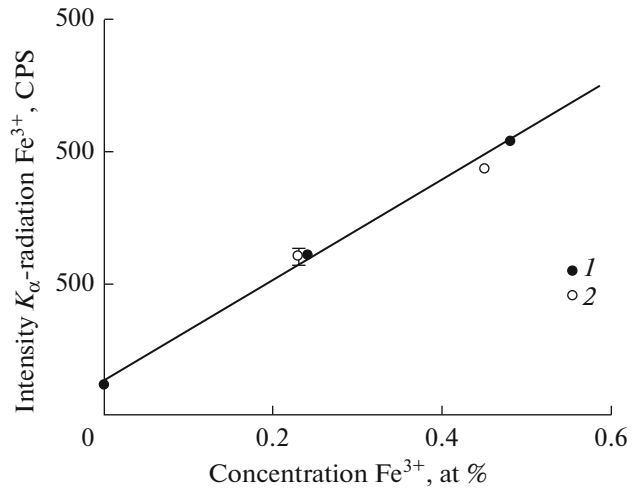


Fig. 2. Dependence of the K_{α} -radiation intensity of Fe on the atomic fraction of iron introduced into $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass as the only additive in the form of a Fe_2O_3 oxide (1) or in the composition of the standard sample of chamotte (2); the solid line is the calibration curve constructed according to the data for Fe_2O_3 .

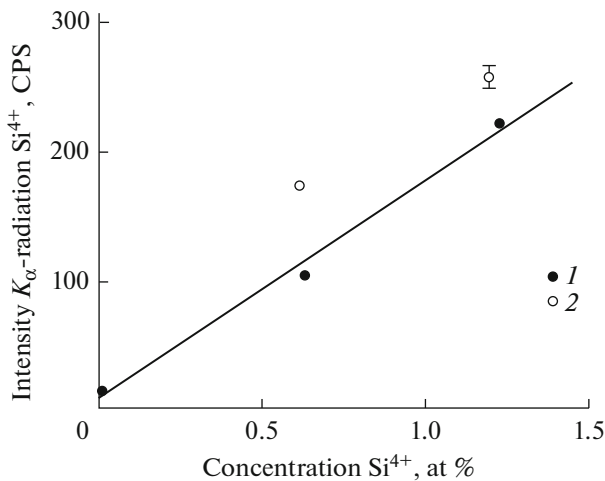


Fig. 3. Dependence of the K_{α} -radiation intensity of Si on the atomic fraction of silicon introduced into $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass as the only additive in the form of SiO_2 oxide (1) or in the composition of the standard chamotte sample (2); the solid line is the calibration curve constructed according to the data for SiO_2 .

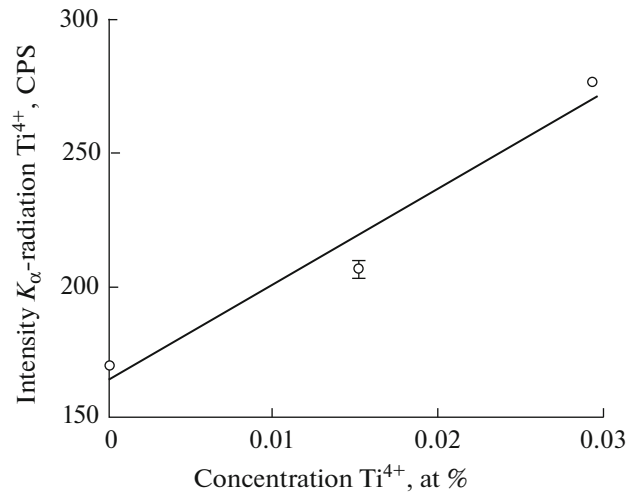


Fig. 4. Dependence of the K_{α} -radiation intensity of Ti on the atomic fraction of titanium introduced into $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass in the composition of the standard chamotte sample.

glass as the only additive was linearly dependent on its atomic fraction (Figs. 1–3). If several elements were injected into the glass (standard sample of chamotte), the dependence of the radiation intensity on the atomic fraction of each of them (except iron) deviated considerably from linearity (Figs. 3–5). Although this relationship was linear for aluminum from the composition of the standard sample, it had an inverse nature: the intensity of radiation decreased with an increase of the aluminum content in the glass (Fig. 6).

All these results are obtained upon irradiating the polished surface. If an untreated surface was irradiated, the intensity of X-ray fluorescence was slightly higher, but the intensity ratio was maintained (Table 1).

RESULTS AND DISCUSSION

The deviation from the calibration curves of the intensity values of the X-ray fluorescence of the elements introduced into the lithium borate glass of the standard sample can be explained by the mutual influ-

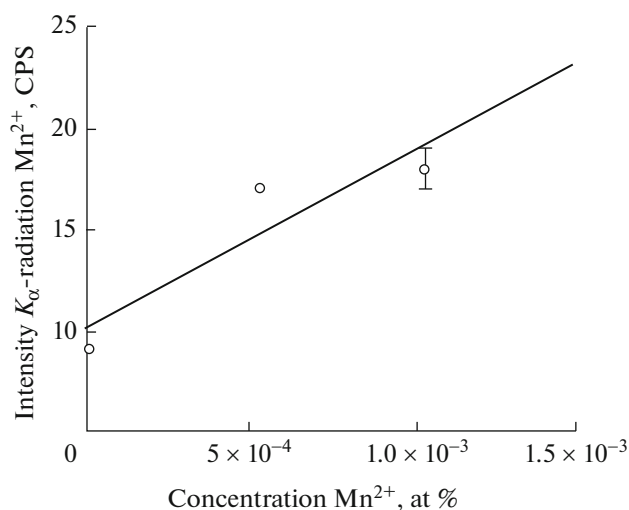


Fig. 5. Dependence of the K_{α} -radiation intensity of Mn on the atomic fraction of manganese introduced into $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass in the composition of the standard chamotte sample.

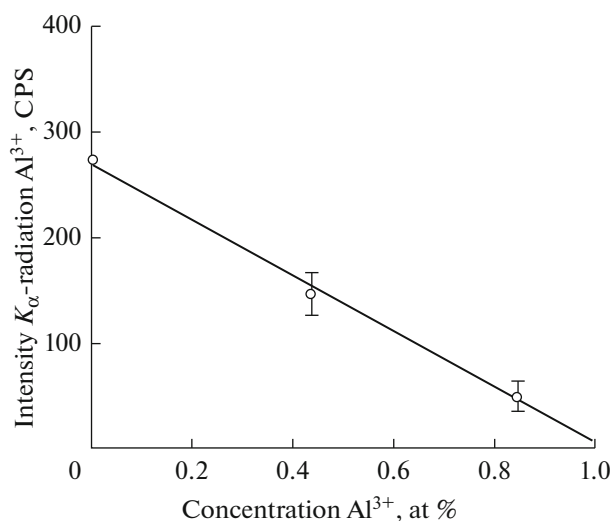


Fig. 6. Dependence of the K_{α} -radiation intensity of Al on the atomic fraction of aluminum introduced into $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass in the composition of the standard chamotte sample.

ence of the components of the standard sample [1, 2]. In this case, the intensity of the lighter elements may be overstated, and the intensity of the heavier elements may be understated. This is due to the wider spectrum range of the braking radiation of the X-ray tube, causing the fluorescence of light elements, as well as the partial absorption of the fluorescent emission of heavy elements by the light elements.

The inverse dependency of the intensity of the K_{α} -emission of Al on the aluminum concentration is probably explained by the elevated level of aluminum in the background, characteristic for the SRM-25 spectrometer, since it is formed not only by the scattering of the primary radiation on the sample but also by the $L_{\beta 2}$ -radiation of rhodium—the anode material of the X-ray tube [12]. The surface layer of glass in this case serves as an absorption filter, weakly absorbing the K_{α} -rays of Al and the much stronger $L_{\beta 2}$ -radiation of Rh. Increasing aluminum concentration in the glass leads to an increase of the absorption properties of the surface layer and a reduction of the fraction of the $L_{\beta 2}$ -

radiation of Rh entering the counter. Reducing the fraction of $L_{\beta 2}$ -radiation of Rh entering the counter at low aluminum concentrations is not compensated by an increase in the intensity of the K_{α} -emission of Al; thus, the total irradiation will decrease. At higher concentrations of aluminum, the $L_{\beta 2}$ -radiation of Rh will be completely absorbed, and the intensity of fluorescent emission of aluminum with an increase in its concentration will also increase.

We also note the lack of correlation between the intensity of the K_{α} -radiation of V and the intensity of the K_{α} -radiation of Al in glass doped with vanadium oxide: an increase in the intensity of the characteristic vanadium emission by $\sim 10^2$ does not lead to an increase in the intensity of the characteristic radiation of aluminum (Table 2).

This fact can be considered as proof of the absence of a significant dissolution of the aluminum crucible in the melt of glass containing vanadium oxide.

It follows from Fig. 1 that the calibration curve for V^{+5} can be used to determine the concentration of the vanadium ions of other oxidation states, V^{3+} and V^{+4} , which is explained by the weak influence of the outer (valence) electrons on the X-ray fluorescence of vanadium ions.

The higher fluorescence intensity upon irradiation of the unpolished surface (Table 1) is due to the lower dispersion of the primary radiation by such a surface, since it is less rough than the polished surface, exposed to abrasive materials during processing.

Table 1. The intensity of the X-ray fluorescence of vanadium upon exposure by a polished and untreated glass surface, CPS

No.	V content in glass, at %	Treatment technique of surface	
		grinding and polishing	without treatment
1	0.06	216	350
2	0.28	1054	1202
3	0.56	1762	2115

Table 2. Intensity of the K_{α} -radiation CPS of Al and V in $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3 : \text{V}_2\text{O}_5$ glass

No.	Type of radiation	V_2O_5 content, wt %			
		0	0.4	2	4
1	VK_{α}	18 ± 0.3	223 ± 2	971 ± 172	1690 ± 211
2	AlK_{α}	269 ± 83	223 ± 54	179 ± 99	226 ± 91

CONCLUSIONS

The intensity of the X-ray fluorescence radiation of the elements injected into lithium borate glass $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ in the form of oxides is linearly dependent on the atomic fraction of these elements; therefore, to obtain calibration curves—graphs and regression equations—one can use a small number of reference samples. The obtained calibration characteristics can be used in the analysis of glass doped only by this element. If along with it other elements are present in the glass, the accuracy of the analysis can be significantly understated.

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