

X-Ray Fluorescence Determination of the Boron Content in Lithium Borate Glasses

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Abstract—A method for the X-ray fluorescence determination of the boron content in lithium borates used for preparing glasses for detecting ionizing radiation is proposed. The measurements are carried out on an S8 Tiger X-ray spectrometer. Sample preparation consists of fusing lithium borates (7.5 g) with a rock sample (0.5 g) and forming a glass disk. The error estimate for boron is 0.2 wt % with the boron content in the range from 21.7 to 27.2 wt % corresponding to the range of content in stoichiometric lithium borates from metaborate to tetraborate.

Keywords: X-ray fluorescence analysis, lithium borates, boron determination

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INTRODUCTION

Lithium tetraborate and triborate doped with rare earth metals are used as scintillators for detecting gamma radiation [1, 2] and thermal neutrons [3]. Both polycrystalline powders and glasses are used as detectors. Borate glasses are considered as promising materials for manufacturing detectors of ionizing radiation [4, 5] and neutrons [3]. The technology for manufacturing glasses based on lithium borates is relatively simple and makes it possible to create detectors of various shapes and sizes. Glasses based on lithium tetraborate are optically transparent in a wide wavelength range, are not hygroscopic, and are stable chemically and in terms of temperature [3, 5]. These properties favorably distinguish glass detectors and make their study relevant.

The boron in borate glasses is determined using classical methods of “wet chemistry” [6, 7] with titrimetric or photometric termination, by optical and mass spectrometry with inductively coupled plasma and neutron activation analysis, a brief overview of which is contained in [8]. The X-ray fluorescence method of analysis is also used to control the composition of borate glasses (borophosphate, barium-lead, etc.) [9–14]. X-ray fluorescence analysis does not require sample decomposition in acids or the preparation of solutions and has the advantage of relatively low sample preparation costs. It is difficult to use this method to determine boron [9–12] because of the extremely low yield of the X-ray fluorescence of boron

(about 0.001) and, accordingly, a weak analytical signal, as well as because of the high values of the coefficients of the attenuation of the BK_{α} -line radiation (several thousand cm^2/g) and, as a consequence, the effect of the surface quality due to the absorption of boron radiation in the micrometer-scale layer of the substance. Methods for controlling the composition of borates were also proposed, using the signal of the X-ray tube radiation scattered in the sample, which responds to the change in the average atomic number of the substance [15, 16]. Such methods [15, 16] of the indirect determination of the composition of lithium borates can be applied in the presence of a priori information about the limited qualitative elemental composition. Sánchez-Ramos et al. [11] give an estimate of the error in determining boron in lead-barium glasses of 0.7 rel % (0.3 wt %) at a boron oxide content of 40.8 wt %. Kikongi et al. [12] give an estimate of the error of 0.7 wt % at a boron content in the range of 0–21.5 wt % in a powder mixture of sodium tetraborate. Based on the data from [11, 12], it is difficult to draw a conclusion about the error in determining boron in the range of compositions of lithium tetraborate and triborate (25.6–27.1 wt %).

The aim of this study is to develop a method for the X-ray fluorescence determination of boron and estimate the error of its determination to control the composition in the synthesis of glasses of lithium tetraborate and triborate.

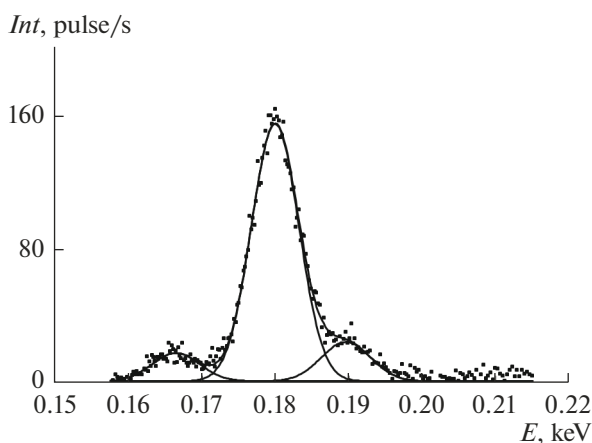


Fig. 1. X-ray spectrum in region of BK_{α} -line. The points in the figure correspond to measurements; solid lines are the decomposition of the spectrum into three Gaussians.

EXPERIMENTAL

Measurement equipment and conditions. The measurements were performed on an S8 Tiger X-ray fluorescence spectrometer (Bruker AXS, Germany), with an X-ray tube with a rhodium anode and a Soller X-ray optical scheme. Spectrum measurements in the analytical K_{α} -boron line regions were drawn using a collimator with a divergence of 1° and a flow-through gas-filled argon-methane detector at a tube voltage and current of 30 kV and 120 mA. The spectrometer is equipped with an XS-C analyzer crystal (synthetic multilayer structure with an interplanar spacing of $2d = 120 \text{ \AA}$) for measuring the K_{α} -carbon line. The XS-C crystal analyzer is not the optimal one offered by the manufacturer of the spectrometer for recording the BK_{α} -line, but allows us to measure the spectrum in the area of interest. Figure 1 shows the spectrum in the region of the BK_{α} -line measured for a pressed powder sample of lithium tetraborate. As noted in [12], in the spectrum, in addition to the main peak corresponding to the radiation energy of the BK_{α} -line, there are two relatively weak peaks of satellite lines. The intensity at the maximum of the main peak is approximately 160 pulses/s, and a measurement exposure of 300 s provides a statistical measurement error of less than 0.5 rel. %. The background measurements were carried out on the right and left in the region outside the boundaries of the satellites approximately corresponding to energies of 0.16 and 0.2 keV. The spectrometer's software allows us to optimize the measurement time of the line and background intensity in such a way as to ensure the specified statistical error. The cumulative measurement time at the peak of line BK_{α} and background measurement positions was about 7 min. Apart from line BK_{α} , the oxygen line OK_{α} was mea-

sured using an XS-55 analyzer crystal ($2d = 55 \text{ \AA}$) to take into account the possible influence of boron on the analytical signal as a result of the imposition of the 3rd order of the reflection of the OK_{α} -line, which was noted in [9], but was not taken into account in [12]. Our spectrometer fails to record the third-order reflection of the oxygen line in the sample (MgO) that does not contain boron.

Materials and sample preparation. We had at our disposal samples of commercial fluxes of stoichiometric lithium borates from various manufacturers used for homogenization by the fusion of rocks during XRF: lithium metaborate (LiBO_2), Sigma-Aldrich; two samples of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), Novosibirsk Plant of Rare Metals and Fluxana; two mixtures (67 wt % $\text{Li}_2\text{B}_4\text{O}_7$, 33 wt % LiBO_2), Chemphys and X-illuminas Flux BGV Lab; and synthesized samples of polycrystalline lithium triborate LiB_3O_5 tested by X-ray phase analysis. The samples were calcined at 600°C to remove hygroscopic and constitutional water. The weight loss upon calcining the samples was less than 0.5 wt %. Unlike lithium tetraborate and triborate, lithium metaborate partially crystallizes on cooling and does not form a sufficiently homogeneous glass. For the preparation of glasses in the range of compositions from lithium metaborate to triborate, the method described in [17] was used, which was used to determine the composition of rocks in the laboratory of the Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences. Weighed portions of fluxes (7.5 g) were fused with a rock sample (500 mg). The standard sample of the composition of garnet-biotite plagiogneiss (GBPg-1, the sum of glass-forming oxides SiO_2 and Al_2O_3 is approximately 80 wt % and the amount of alkali oxides K_2O and Na_2O of 5.8 wt %), which forms glass with the mentioned fluxes. Glass disks 32 mm in diameter were prepared by being cast into platinum molds after fusion in platinum crucibles in a TheOX electric furnace (Claisse, Canada) at a temperature of 1050°C .

The preparation of pressed powder emitters leads to the need to control or stabilize the particle size distribution of the powders due to the dependence of the intensity of the BK_{α} -line on the surface quality. Grinding lithium tetraborate powder in a steel container of a ball mill for 3–6 min leads to an increase in intensity of the BK_{α} -line by 10–20 rel. % and this deviation is greater than the difference in the boron content in lithium tetraborate and triborate. The increase the intensity of the BK_{α} -line, in our opinion, is due to the decrease in the size of the roughness of the sample surface and a weakening of the screening of boron radiation by particles on the surface at a radiation takeoff angle of 45° of the used spectrometer.

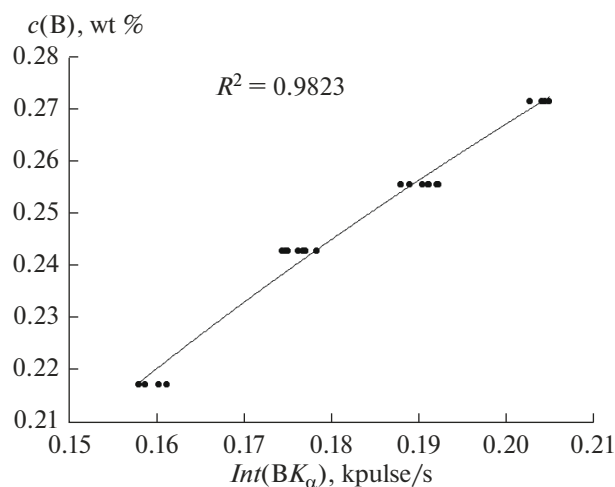


Fig. 2. The relationship between boron content $c(B)$ and fluorescence intensity of the BK_{α} -line $Int(BK_{\alpha})$. The points correspond to the measurement results, the solid line is the approximation by a polynomial of the second degree.

RESULTS AND DISCUSSION

To construct the calibration characteristic, two series of glass samples (12 samples) were prepared from the mentioned lithium borates. Each sample was measured twice. Figure 2 shows the measurement results and an approximation of the relationship between the boron content $c(B)$ and fluorescence intensity of the BK_{α} -line $Int(BK_{\alpha})$.

Table 1 shows the possible equations of the calibration characteristic, the coefficients of which are significant compared to their error at a confidence level of 95% (Student's test > 2.06). The residual standard deviation (SD) of the regression equation for the boron content in lithium borates ranging from 21.73 wt % (metaborate) to 27.17 wt % (triborate) was estimated. The significant effect of variation in the oxygen content (Table 1, third row) can be due to both the super-

position of the OK_{α} -line, and the effect of secondary boron fluorescence arising from the excitation of oxygen radiation in the sample.

The estimate of the boron determination error given in Table 1 is comparable with the estimate given in [11] (0.3 wt %), and less by factors of two and three than the estimate in [12] (0.7 wt %) for the ranges of the boron content that differ from the range in this study and less than the estimate of 0.6 wt % given in [16] for the coinciding range.

The glass samples used to construct the calibration functions (Table 1) were also used to construct the calibration function in the method described in [16], based on measuring the intensity of the X-ray tube radiation scattered in the sample. The standard deviation of boron determination using a calibration function based on measuring the scattered radiation from a tube was 0.5 wt % and this estimate is 2.5 times greater than the smallest error estimate in Table 1. As an example of comparing the two methods, lithium borate of unknown origin was analyzed. The proposed method gives an estimate of the boron content of 23.82 (0.18) wt % (the difference between two parallel determinations is given in parentheses) and the method [16] based on measuring the scattered radiation leads to a close value of 23.76 (0.18) wt %.

CONCLUSIONS

The proposed method for the X-ray fluorescence determination of boron in glasses prepared from lithium borates provides an error in the determination of the content at the level of 0.2 to 0.3 wt % in the range of the boron content corresponding to the content in stoichiometric lithium borates from 21.7 to 27.2 wt %, and can be recommended for monitoring the composition of glasses used for manufacturing ionizing radiation detectors.

Table 1. Equations of calibration characteristics for boron determination

	The equation	SD, wt %
Line	$c(B) = 0.0335 + 1.1730Int(BK_{\alpha})$	0.28
2nd degree polynomial	$c(B) = -0.2215 - 7.779Int(BK_{\alpha}) + 3.9984Int^2(BK_{\alpha})$	0.24
Linear regression with OK_{α} -line	$c(B) = 0.2901 + 0.8924Int(BK_{\alpha}) - 0.014142Int(OK_{\alpha})$	0.20

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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