===== **PHYSICS** =====

X-Ray Photoelectron Study of Charge States
for Bismuth and Aluminum Atoms in Glasses Luminescent
in the Infrared Region

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INTRODUCTION

The necessity to extend the spectral range of optical-fiber communication lines stipulates the active usage of the second telecommunication transparency window (1.2–1.35 μm). However, at present, efficient lasers and amplifiers based on active light guides made of quartz glass, which are consistent with standard telecommunication fibers, are absent for this spectral range.

Recently, information has appeared that the wide-band luminescence was observed in the near-IR spectral range (1100–1700 nm) in some (silicate, germinate, phosphate, and borate) glasses doped with bismuth and fabricated by melting charge in a crucible [1–4]. In addition, with the use of the method of metalorganic chemical vapor deposition (MOCVD), fiber light guides having analogous spectroscopic characteristics were fabricated on the basis of aluminosilicate glass doped with bismuth. By virtue of their spectral position (1050–1200 nm), bandwidth (150–200 nm), and long luminescence lifetime (about 1 ms), these light guides turn out to be rather promising for constructing tunable and femtosecond-range lasers, as well as wide-band amplifiers. In particular, continuous-wave and pulsed lasers (with Q-factor modulation and with mode synchronization) based on light guides of this type were made successfully [4–6].

Studies of this problem have generated a number of hypotheses on the nature of luminescent bismuth centers and on the specific role of aluminum. However, none of them was convincingly confirmed. One of the reasons is the lack of experimental data that could exhaustively characterize the objects under study. Basically, glasses and light guides are studied by methods of the absorption luminescence spectroscopy. In addition, several attempts to study glasses by methods capable of determining the symmetry of active centers and the structure of their nearest surrounding, including the EPR [7, 8], NMR [9], and EXAFS [10, 11] techniques are known.

In this study, we used the method of the X-ray photoelectron spectroscopy (XPS), which has allowed us to determine the charge state of all atoms. Of primarily interest was the state of Bi atoms, since the data found in the literature on its oxidation degree had been rather contradictory.

EXPERIMENTAL

Phosphate glasses were produced by melting in alundum or platinum crucibles (at a melting temperature of about 1350°C). Silicate glasses were fabricated by chemical deposition from the gas phase in a quartz-glass reference tube (MOCVD technology, the porous layer being saturated with a solution of bismuth salts) [4].

Silicate glasses (quartz glass doped with Al, P, and Bi) were the blank cores for fiber light guides. The synthesis temperature attained 1900°C. For these studies, cores 1.4 mm in diameter were drilled out from blanks.

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Table 1. Chemical composition of samples according to the EPMA data (at. %) and the absorption coefficient (dB m^{-1}) in the luminescent bismuth-center band near 500 nm

Sample no.	Si	P	Al	Bi	Na + Ca	REE	O	Absorption coefficient
1	–	25.25	2.87	0.43	–	1.36 (Y)	70.1	100
13	–	24.64	2.66	0.54	–	2.31 (Ce)	69.85	<10
23	–	24.55	2.59	0.56	–	2.48 (La)	69.82	2000
27	0.3	22.4	0.44	0.32	7.2	2.64 (La)	66.7	–
U-1	30.5	2.5	–	0.013	–	–	67	100
U-3	30	–	4	<0.01	–	–	66	45
U-12	31	–	2.8	<0.01	–	–	66.2	450
U-15	31.3	–	2.5	<0.01	–	–	66.2	75

Table 2. Composition of phosphate glasses (sample 1) expressed in atomic fractions with respect to the atomic concentration

Method	Processing	P	Al	Bi	Y	O (including OH groups)
EPMA	–	1	0.11	0.017	0.054	2.77
XPS	Washing by ethanol	1	0.09	0.01	0.12	3.03/1.44
XPS	Ar$^+$ 2 min	1	0.09	0.01	0.13	2.86/0.73
XPS	Ar$^+$ 12 min	1	0.13	0.01	0.17	2.41/1.12

Samples for the measurement of XPS spectra were prepared from fine powders triturated in an agate mortar. The samples were used in the form of either dense thick layers with a mirror surface, which were pressed into indium on a titanium substrate, or tablets stuck with Scotch tape to the titanium substrate. In some cases, the powder could be studied as deposited directly onto the Scotch tape. We also used samples in the form of polished glass plates. These plates were fixed by a foil to a conducting substrate. Initially, all samples were studied without preliminarily purifying their surfaces by the bombardment with argon ions. Then, the samples were bombarded for a short time (2 min) with Ar$^+$ ions in order to remove surface layers of carbon-containing contaminants. To this end, an argon gun was employed (the voltage, the ion current, and the spot diameter were, respectively, $U = 2.5$ kV, $I = 40$ mA, and $d = 1.5$ cm, for which the etching rate was $V = 3–10$ Å/min). It was found that under these experimental conditions, processing the sample surface results in removing surface hydrocarbonsup to a depth of 20 Å. In some cases, the ion etching time was increased to 12 min.

The XPS spectra of the samples under consideration were mostly obtained on an I? 5950A electrostatic spectrometer using monochromatic Al$K_{\alpha1.2}$ (1486.6 eV) radiation at a residual pressure of 1.3×10^{-7} Pa at room temperature. We also employed an MK II VG Scientific spectrometer using the same nonmonochromatic Al$K_{\alpha1.2}$ (1486.6 eV) radiation. The values of the electron binding energies E_b (eV) are given with respect to

that of C1s electrons for hydrocarbons on the sample surface. This value was assumed to be 285.0 eV. The measurement error for binding energies and bandwidths was 0.1 eV. For measured relative intensities, the error is about 10%.

Since the XPS method makes it possible to study only the near-surface layer with a thickness of several nanometers, it is necessary to compare the results of XPS measurements to the data obtained by bulk methods of analysis, doe example, the electron-probe microanalysis (EPMA), in order to substantiate the adequacy of the employed method. The quantitative elemental EPMA measurements were performed for all samples using a JEOL JSM-5910LV scanning microscope equipped with an Oxford Instruments INCAEnergy EDS energy-dispersive microanalyzer. For this method, the depth of the probed layer is about 1 μm and the relative accuracy of the element concentration determination is on the order of 10%. The results obtained are given in Table 1, where the optical absorption coefficient for a band near 500 nm is also indicated which corresponds to the luminescent bismuth centers and qualitatively characterizes their concentration.

The XPS method for phosphate glasses gave the results consistent with the EPMA data. In other words, the surface studied by the XRES method on the whole corresponds to the bulk composition. The compositions of some phosphate glasses, which were determined by the two methods, are given in Table 2. The yttrium content measured by the XPS method is higher than that found by the EPMA method because yttrium atoms are

Table 3. Composition of the U-1 silicate glass in atomic fractions with respect to the concentration of Si atoms

Method	Si	Al	Bi	P	O
EPMA	1	0	0.0004	0.064	2.18
XPS	1	0	0.0069	0.027	2.49

concentrated at the surface due to the formation of the $Y(OH)_3$ hydroxide on the sample surface since yttrium reacts with water vapors.

The results of determination of the chemical composition for U-1 sample are presented in Table 3. In this case, the two methods give noticeably different results. This is probably caused by an inhomogeneous distribution of the doping admixtures along the silicate-glass blanks (the samples studied by the two methods were cut from different parts of blanks). By virtue of the large volatility of bismuth compounds and the developed glass surface, this statement is especially true for the bismuth concentration in samples prepared udig the MOCVD process.

EXPERIMENTAL RESULTS

Table 4 presents data obtained for a number of chemical compounds of Bi. These compounds are taken as calibration samples with the well-known charge state (valence) of bismuth (Bi(0) for metallic bismuth; Bi(III) for Bi_2O_3, $Bi(NO_3)_3 \times 5H_2O$, and $BiPO_4$; and Bi(V) for $NaBiO_3$). As can be seen, the binding energy for $Bi4f_{7/2}$ in metallic Bi is 157.3 eV, whereas for Bi(III), it is 159.7 eV. At the same time, for compounds of Bi(V), approximately the same values 159.8 ± 0.6 eV of $Bi4f_{7/2}$ energy were obtained as well as for compounds of Bi(III). This is a quite expected

result, since only films of Bi(III) compounds could be stable.

The data on binding energies for the samples of phosphate and silicate glasses are presented in Table 5. It should be noted that the O1s spectral line contains a component close to 534 eV, which indicates the existence of hydroxy (OH^-) groups entering into the composition of the yttrium hydroxide and, apparently, water. This should be expected because oxides of rare-earth elements (REEs), as was noted above, are easily hydrolyzed on the surface.

In glasses based on P_2O_5-Al-REE-Bi (samples 1, 13, 23, 27), the binding energy of $Bi4f_{7/2}$ (160.7 ± 0.5 eV) exceeds that in compounds of Bi(III). With a great degree of determinacy, this implies that the positive charge on Bi atoms in these glasses exceeds that in compounds of Bi(III). In principle, the values obtained for $Bi4f_{7/2}$ in phosphate glasses are strongly different compared to those for Bi(III) so that we can speak about the elevation of the formal oxidation degree up to Bi(V). In addition, in phosphate glass almost not containing aluminum (sample 27) along with Bi(V), the signal corresponding to metallic bismuth is registered, namely, to Bi(0) (157.9 eV).

However, in silicate glasses (samples U-1, U-3, U-12, and U-13) the value of the binding energy for $Bi4f_{7/2}$ (159.4 ± 0.2 eV) coincides with that in compounds of Bi(III) (Tables 4, 5). This probably corresponds to the fact that the bismuth content in silicate glasses was two orders of magnitude smaller than that in silicate glasses (at comparable concentrations of Al). If we assume the content of Si to be equal to unity, then the contents of Bi atoms in samples U-1, U-3, U-12, and U-15 attain $(6.9, 3.3, 0.25,$ and $0.82) \times 10^{-3}$, respectively. The listed values of the total concentration of Bi atoms do not correlate with the absorption coefficient and, hence, with

Table 4. Electron binding energies in chemical compounds of Bi

Sample	Bi valence	$Bi4f_{7/2}$	Na1s	O1s
Bi_2O_3, powder	Bi(III)	159.7		530.0
$Bi(NO_3)_3 \times 5H_2O$, $E_b(N1s) = 407.4$	Bi(III)	159.8		530.3 532.1 533.5
$NaBiO_3$, powder	Bi(V)	160.4	1071.8	531.5
$NaBiO_3$, powder + Ar^+ 3 min	Bi(V)	160.0	1071.8	531.0
$NaBiO_3$, powder + Ar^+ 3 min + oil	Bi(V)	159.2	1071.8	530.2
Bi, metallic plate, unpurified	Bi(0)	159.3		530.4 532.0
Bi, metallic plate, mechanically purified	Bi(0)	157.3*		none
$BiPO_4^{**}$	Bi(III)	160.2		531.6 533.5

* Corresponds to metallic Bi.
** the value of $P2p$ is 134.0 eV.

Table 5. Electron binding energies (eV) in glasses

Sample, processing	P2p P2s	Al2p Al2s	Bi4$f_{7/2}$	Ce3$d_{5/2}$ La3$d_{5/2}$	Na2s Na1s	K2$p_{3/2}$	Ca2$p_{3/2}$	O1s	Si2p Si2s
1, Ar$^+$ 2 min	134.9 192.5	75.7 120.4	160.9		63.7 1072.4	293.5	348.1	532.6 534.5	
2, initial	134.6 192.3	75.5 120	160.7		63.6 1072.1	293.2	347.7	531.6 533.3	
2, Ar$^+$ 2 min	135.2 192.5	75.7 120.8	161.0		64.0 1072.5	293.5	348.1	532.2 533.9	
2, Ar$^+$ 12 min	136.0 192.3	75.9 121.4	160.9		64.2 1072.7	293.7	348.4	532.7 534.4	
3, Ar$^+$ 2 min	135.0 192.4	75.5 120.6	159.4		63.8 1072.6	293.6	347.2	532.3 534.1	
13 (Ce–Bi)	134.2	75.4	160.6	884.4 886.4	1072.3	293.1		531.9 533.6	
13 (Ce–Bi), Ar$^+$ 1 min	134.6	75.4	160.5	884.2 886.2		293.3		531.9 533.6	
13 (Ce–Bi), Ar$^+$ 5 min	134.8	75.7	160.9	884.7 886.7		293.6		532.1 533.6 535.4	
23 (La–Bi)	134.6 191.8	75.3	160.5	836.7 839.1	1072.2			531.9 533.5	
23 (La–Bi), Ar$^+$ 1 min	134.9 192.1	75.5	160.6	836.6 839.3	1072.2			531.9 533.7	
23 (La–Bi), Ar$^+$ 5 min	135.6 192.6	76.3	161.4	837.1	1072.2			532.6 534.2	
27 (glass without Al)	134.6		157.9* 160.6	836.3 839.3	1072.2		348.0	532.0 533.8	
U-1	135.3		159.7					533.1	103.7 154.9
U-3**		75.2	159.1					533.1	103.6 154.6
U-12		75.2	159.4					533.0	103.6 154.5
U-15		75.3	159.3					533.0	103.6 154.6

 * Corresponds to metallic Bi.
** normalization to Si2p = 103.6 eV.

the concentration of scintillating bismuth centers (see Table 1).

It is necessary to note that the energy of Al2p in both phosphate and silicate glasses (Table 6) is elevated compared to the majority of oxygen compounds of aluminum (e.g., about 74.8 eV for Al$_2$O$_3$) [12]. However, in glasses containing aluminum, its elevated coordination (apparently corresponding to the elevated charge state) is known rather well (see, e.g., [9, 13] and references therein). We can assume that the presence of Al in glasses promotes the accumulation of the positive charge on a Bi atom and the luminescence. The available data for the nonluminescent glass (sample U-27, Table 2) confirm the validity of this assumption. Nominally, this glass was not doped with aluminum (0.44 at. % of Al are

stipulated by cooking this glass in an alundum crucible) in which the reduction of Bi up to the metallic state is observed, although the chemical conditions for cooking this glass and other glasses differ weakly from each other. This corresponds to the conclusions made in [9], where the considerable positive effect of aluminum

Table 6. Binding energies (eV) for Bi4$f_{7/2}$ and Al2p

Spectral line, eV	Metallic Bi(0)	Compounds Bi(III)	Phosphate glasses Bi(III–V)	Silicate glasses
Bi4f	157.6	160.2–159.3	160.6	160.1–159.3
Al2p		74.5	75.4	75.2

atoms in their hexa-coordinated systems (i.e., in the state with a large positive charge compared to the tetra-coordinated state) on the formation of scintillating Bi centers was shown.

While discussing the problem of the electron state of Bi atoms responsible for the luminescence, which was studied by the XPS method, we should allow for two facts. First, it should be noted that the concept of the oxidation degree is conditional. The oxidation degree is the experimentally unobservable quantity and depends on LCAO coefficients in the molecular-orbital method. In quantum chemistry, the oxidation-degree concept is entirely absent. Nevertheless, in a number of cases, this concept is fruitful and can be understood on the basis of the modern theory of chemical binding [14].

In the framework of the concept of a molecular orbital as a linear combination of atomic orbitals (LCAO), the oxidation degree for Bi atoms depends on the relation between the LCAO coefficients. In principle, continuous transition is possible between states of Bi(III) and Bi(V), although the accumulation of quantitative differences can lead to a qualitative jumplike variation of glass properties:

$$\alpha_1(\text{Bi}6s) + \beta_1(\text{O}2p),\ \alpha_1 > \beta_1,\ \alpha_1 < \beta_1 \text{ (occupied orbital)},$$

$$\alpha_2(\text{Bi}6s) + \beta_2(\text{O}2p),\ \alpha_2 < \beta_2,\ \alpha_2 > \beta_2 \text{ (free orbital)}.$$

For an unoccupied level described by the function $\alpha_2(\text{Bi}6s) + \beta_2(\text{O}2p)$, $\alpha_2 > \beta_2$ for Bi(V) and $\alpha_2 < \beta_2$ for Bi(III), i.e., the level depending on the formal oxidation degree, the probability of the electron excitation onto a given level is different. By virtue of this fact, in discussing the electron state of Bi atoms responsible for the luminescence, we should allow for two arguments. First, the oxidation-degree concept is conditional. Second, it is necessary to take into account that the XPS spectra characterize all Bi atoms in the sample under study, whereas only their fraction takes part in the luminescence. This fraction is relatively small since, due to the significant difference in the electron structure, these atoms must have different binding energies for $\text{Bi}4f_{7/2}$.

However, we observe neither additional maxima nor an increase in the $\text{Bi}4f_{7/2}$-line width. With allowance for the accuracy of the XPS method, the concentration of luminescent bismuth centers in the samples under study does not exceed 5% of the total bismuth concentration.

Thus, atoms of Bi and Al in the studied phosphate glasses have a high positive effective charge compared to that in compounds of Bi(III) and Al(III). This allows us to formally consider Bi(V) as the ground state of bismuth. The charge of Al is also elevated in silicate glasses.

We also note the absence of quantitative correlation between the luminescence intensity and the concentration of Bi, as well as the unperturbed state of the $\text{Bi}4f_{7/2}$ line compared to the bismuth compounds in which the luminescence is absent. This shows that only a negligible fraction of bismuth atoms present in glass participates in the luminescence. The fraction of luminescent bismuth centers and the state of bismuth atoms in them are still unknown.

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