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Abstract

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ON THE NATURE OF THE “FLUCTUATION BANDS OF BORIC ACID”

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It is well known that flames, when boron or its compounds are introduced into them, become colored green. This green luminescence is due to a number of so-called “fluctuation bands of boric acid” (^{1}), which are located in the region from 3700 to 6800 Å and are used for the spectrophotometric analysis of boron. Although the fluctuation bands were first discovered as early as the last century (^{2}), their nature is still unknown. The bands have been attributed to boric acid (^{2}), to the radicals BO (^{3}), BOH (^{4}), and to the molecule B_2O_3 (^{5}, ^{6}). In the work (^{7}), which was carried out in our laboratory, it was shown, on the basis of an analysis of isotope shifts in the edges of the fluctuation bands, that the assignment of these bands to the BO radical (^{3}) is incorrect and that the molecule giving the “boric acid” spectrum contains no hydrogen in its composition, but is a polyatomic oxygen compound of boron of composition B O . If the fluctuation bands were due to a molecule containing two boron atoms, for example the B_2O_3 molecule, as asserted by Soulen, Sthapitanonda, and Margrave (^{5}, ^{6}), then, with an isotope B^{10} content of about 50%, there should be three systems of band heads in the spectrum, due to three isotopic molecules $B_2{}^{10}O_3$, $B^{10}B^{11}O_3$, and $B_2{}^{11}O_3$.

Using a discharge tube with a hot hollow cathode (^{7}) on a DFS-3 spectrograph with a dispersion of 2 Å/mm, we recorded the emission spectra of the fluctuation bands in the regions 5470, 5800, and 6300 Å as a function of the isotopic composition of boron oxide (the concentration of the isotope B^{10} was 18, 55, and 90%). Figure 1 (see insert, p. 68) shows the isotope shifts in the 5470 Å band. In the spectrum only two systems of isotope band heads are visible, which may be due to a molecule containing one boron atom. True, one cannot exclude, although it is unlikely, the possibility that the isotope shifts between the molecule $B^{10}B^{11}O_3$ and any of the molecules $B_2{}^{10}O_3$ or $B_2{}^{11}O_3$ are so small that we do not observe them.

Since the isotope bands do not give an unambiguous solution concerning the nature of the fluctuation bands, the emission and absorption spectra of vapors over boric anhydride were investigated in the visible and infrared regions at temperatures of 1200–1550°C in inert (He, Ar, N_2), oxidizing (O_2), and reducing (H_2) atmospheres and in the presence of water vapor.

Fig. 1

Figure 1: Fig. 1

Fig. 1

Figure 2: Fig. 1

Boron oxide was placed in a tube made of heat-resistant porcelain and heated in a graphite furnace. By means of glass adapters with windows, the tube was connected to a vacuum apparatus, which served for evacuating and filling the system with various gases. Before the start of work, the boron oxide was thoroughly degassed at 1000° under continuous pumping (the heat-resistant porcelain tubes made it possible to attain a vacuum of the order of $1 \cdot 10^3$ mm Hg at 1550°). The temperature was measured inside the tube with a platinum-platinum-rhodium thermocouple or with an optical pyrometer. The emission and absorption spectra in the visible region were recorded on an ISP-22 spectrograph. The absorption spectrum was registered with the aid of a spectrophotometric attach-

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Fig. 1. X-ray diffraction patterns of the compounds Cu_2GeS_3 (1), Cu_2SnS_3 (2), Cu_2GeSe_3 (3), Cu_2SnSe_3 (4), Cu_2GeTe_3 (5), Cu_2SnTe_3 (6)

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Fig. 1. Isotopic shifts in the band λ 5470 Å

···of a Dianov-Klyukov design (8). The emission and absorption spectra in the infrared region were recorded on an IKS-6 spectrometer with an AC amplifier assembled according to Markov’ s circuit (9). Since analysis of the spectra in the visible and infrared regions showed that the emission and absorption spectra coincide completely in all atmospheres investigated, the studies were carried out using absorption spectra.

The literature (5) had noted the interaction of boron oxide with porcelain tubes; therefore, the effect of the tube material on the spectrum of vapors above heated boron oxide was checked. For this purpose a cylinder rolled from platinum foil was inserted into the porcelain tube. However, as experiment showed, this precaution was unnecessary.

Fig. 2. Effect of different atmospheres on the intensity of “fluctuation bands”

Fig. 2. Effect of different atmospheres on the intensity of “fluctuation bands” of absorption at 1500° (gas pressure 250 mm). a –He, –O_2, –H_2

Figure 3: Fig. 2. Effect of different atmospheres on the intensity of “fluctuation bands” of absorption at 1500° (gas pressure 250 mm). a –He, –O_2, –H_2

of absorption at 1500° (gas pressure 250 mm). a –He, b –O_2, v –H_2.

Figure 2 presents the dependence of the intensity of the fluctuation absorption bands on the nature of the atmosphere. In an inert atmosphere, fluctuation bands arise only at temperatures of 1400–1550°, and even then their intensity is very small. The addition of oxygen, even in small amounts (3 mm Hg), sharply increases the intensity of the fluctuation bands; moreover, as the oxygen pressure increases, the intensity of the bands also increases. At atmospheric oxygen pressure, luminescence appears already at 1200°. In the presence of hydrogen, fluctuation bands do not arise at all; moreover, hydrogen quenches luminescence that is already present. Passing water vapor over heated boron oxide causes a strong transport of material as a result of the formation of boric acid, while the fluctuation bands are absent.

A mass-spectrometric study of the vapor above boron oxide ([10,11]) at temperatures of the order of 1300° showed that, in vacuum or in an inert atmosphere, the vapor above boric anhydride consists mainly of B_2O_3 molecules. Therefore the anomalous effect of oxygen on the intensity of the fluctuation bands, compared with an inert atmosphere, indicates that these bands belong to another oxygen-containing compound of boron with a higher oxygen content than the B_2O_3 molecule. In our opinion, this is the BO_2 radical ([12]). Then the increase in the intensity of the fluctuation bands upon addition of oxygen can be explained by the reaction
$B_2O_3 + \frac{1}{2}O_2 = 2BO_2$, and the appearance of fluctuation bands in an inert atmosphere at temperatures of 1400–1500° is due to slight dissociation of boron oxide: $B_2O_3 = BO + BO_2$. Quantitative measurements of the dependence of the intensity of the fluctuation bands on oxygen pressure ([13]) fully confirm that the carrier of the fluctuation bands is the BO_2 radical. This conclusion agrees well with the isotopic shifts discussed above.

In studying the infrared spectra in the region from 3 to 12 μ, we found only one band, at about 2000 cm^{-1}, which is due to vibrations of the double bond $B = O$ in the B_2O_3 molecule ([14]). The intensity of the absorption band at 2000 cm^{-1} is the same in atmospheres of helium, argon, nitrogen, oxygen, and hydrogen, and increases strongly when water vapor is passed through, evidently because of an increase in the concentration of molecules containing the $B = O$ group. In the presence of water vapor, in addition to B_2O_3, such a molecule may also be HBO_2. The fact that oxygen has practically no effect on the intensity of the 2000 cm^{-1} band indicates that the concentration of the BO_2 radical at 1550° is small compared with the concentration of B_2O_3 molecules.

The conclusion we drew in 1958 that the fluctuation bands are due to the radical BO_2 [12] has only just been confirmed by the work of Kaskan and Millikan [15] on the investigation of the intensity of fluctuation bands in trimethyl borate flames.

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Note: Figure translations are in progress. See original paper for figures.