

Interstitial BiO molecule as a broadband IR luminescence centre in bismuth-doped silica glass

V.O. Sokolov, V.G. Plotnichenko, E.M. Dianov

Abstract. Experimental data on absorption and luminescence in optical fibres with a Bi:SiO₂ glass core are compared to experimentally determined and calculated spectroscopic properties of the BiO molecule. The results suggest that the IR luminescence of Bi:SiO₂ glass is due to interstitial BiO molecules. This assumption is supported by quantum-chemical simulation results for a BiO molecule in a ring interstice of the silica glass network.

Keywords: optically active bismuth centres in glass, luminescence.

Bufetov et al. [1] and Firstov et al. [2] have recently measured, for the first time, the luminescence spectra of optical fibres with a silica (SiO₂) core doped only with bismuth oxide (Bi₂O₃), without any other dopants. According to their results, the most characteristic spectroscopic properties of Bi:SiO₂ glass are as follows:

1. Absorption around 1425, 820 and 620 nm and at wavelengths shorter than 450 nm (transition energies near 7020, 12 150 and 16 130 and above 22 200 cm⁻¹, respectively) leads to luminescence around 1430 nm (6990 cm⁻¹).

2. Absorption around 820 and below 450 nm (transition energies near 12 150 and above 22 200 cm⁻¹, respectively) leads to luminescence around 830 nm (12 050 cm⁻¹).

3. At liquid nitrogen temperature, there is also weak luminescence near 910 and 830 nm (transition energies of about 10 990 and 12 150 cm⁻¹, respectively), which can be excited through absorption near 820 and 760 nm (12 195 and 13 155 cm⁻¹), respectively.

4. The lifetimes of the states responsible for the luminescence near 1430 and 830 nm are 640 and 40 μs, respectively.

It is worth noting here that the above absorption and luminescence features of Bi:SiO₂ glass fit well with the known spectroscopic properties of the bismuth monoxide (BiO) molecule [3–5].

In Table 1, we present experimental data from Refs. [1, 2] and assign the observed transitions using spectroscopic data available for the BiO molecule [3–5]. Figure 1 shows the total energy curves obtained for the BiO molecule from configuration interaction calculations with spin–orbit interaction taken into account [5] and corrected for experimental data [3, 4].

The BiO molecule has a low-lying excited electronic state near 7090 cm⁻¹, X₂²Π_{3/2}, with a lifetime of 480 ± 100 μs for

the transition to the ground state [3] (calculated values are 6810 cm⁻¹ and 2700 μs, respectively [5]). The X₂ → X₁ absorption leads to X₂ → X₁ IR luminescence. A characteristic feature of the BiO molecule is that the minimum of the X₂ state almost coincides with that of the X₁²Π_{3/2} ground state (Fig. 1), so the Stokes shift of this luminescence is very small. The strongest absorption bands of the BiO molecule are due to transitions from the ground electronic state to the A₂⁴Π_{1/2} electronic state (the average energy of the 0–0, 1–0, 2–0 and 3–0 transitions from vibrational states of X₁ to the ground vibrational state of A₂ is about 12 200 cm⁻¹, with an average wavelength near 820 nm for a vibrational frequency of about 690 cm⁻¹ in the X₁ state [3, 4]), the H²Π_{1/2} and I⁴Σ_{1/2} states (20 500–22 000 cm⁻¹, or 450–490 nm) and a number of higher energy electronic states (above 25 000 cm⁻¹, or under 400 nm). In addition, calculations [5] predict an absorption band around 16 130 cm⁻¹ (630 nm), due to the transition from the ground state to the A₄⁴Π_{1/2} state, which has a lifetime near 165 μs.

The lowest excited state, X₂, can be populated not only via transitions from the ground state but also via nonradiative relaxation from any of the higher energy states indicated above.

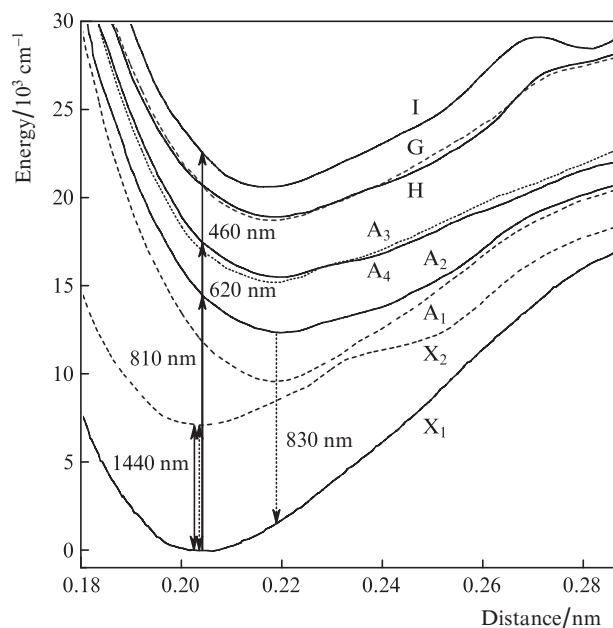


Figure 1. Total energy curves for the lower electronic states of the BiO molecule according to calculation results [5] and experimental data [3] (solid lines: states with a total angular momentum $\Omega = 1/2$; dashed lines: $\Omega = 3/2$; dotted line: $\Omega = 5/2$), and transitions corresponding to absorption (solid arrows) and luminescence (dashed arrows) bands.

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Table 1. Spectroscopic data from Refs [1, 2] and assignment to transitions of the BiO molecule.

Absorption			Luminescence		
Wavelength/nm	Frequency/cm ⁻¹	Transition	Wavelength/nm	Frequency/cm ⁻¹	Transition
1425	7018	X ₁ ² Π _{1/2} → X ₂ ² Π _{3/2}	1435	6969	X ₂ ² Π _{3/2} → X ₁ ² Π _{1/2}
821	12180	X ₁ ² Π _{1/2} → A ₂ ⁴ Π _{1/2}	1430	6993	X ₂ ² Π _{3/2} → X ₁ ² Π _{1/2}
< 450	> 22200	X ₁ ² Π _{1/2} → H ² Π _{1/2} , I ⁴ Σ ⁻ _{1/2} , etc.	1430	6993	X ₂ ² Π _{3/2} → X ₁ ² Π _{1/2}
620	16129	X ₁ ² Π _{1/2} → A ₄ ⁴ Π _{1/2} (?)	1480	6757	X ₂ ² Π _{3/2} → X ₁ ² Π _{1/2}
823	12150	X ₁ ² Π _{1/2} → A ₂ ⁴ Π _{1/2}	833	12005	A ₂ ⁴ Π _{1/2} → X ₁ ² Π _{1/2}
< 450	> 22200	X ₁ ² Π _{1/2} → H ² Π _{1/2} , I ⁴ Σ ⁻ _{1/2} , etc.	830	12048	A ₂ ⁴ Π _{1/2} → X ₁ ² Π _{1/2}
820	12195	X ₁ ² Π _{1/2} → A ₂ ⁴ Π _{1/2}	910	10990	A ₂ ⁴ Π _{1/2} → X ₁ ² Π _{1/2}
760	13158	X ₁ ² Π _{1/2} → A ₂ ⁴ Π _{1/2}	830	12048	A ₂ ⁴ Π _{1/2} → X ₁ ² Π _{1/2}

*The absorption or luminescence wavelength corresponds to transitions involving both the ground and an excited vibrational state of the X₁²Π_{1/2} ground electronic state of the BiO molecule.

On the other hand, a number of radiative transitions from these states are possible, resulting in luminescence. The most likely transition is A₂ → X₁ (energy of about 12005 cm⁻¹, wavelength near 835 nm; lifetime of the A₂ state, 9 ± 2 μs [3]). The Stokes shift is here also small, because of the significant contribution from vibrational excitations of the ground electronic state.

Note that, in experiments with optical fibres [1], markedly longer lifetimes were obtained for the states responsible for the luminescence near 1430 and 830 nm (see above). In general, this is attributable to the significant influence of reabsorption when the absorption and luminescence bands strongly overlap (in lifetime measurements, Bufetov et al. [1] excited luminescence in the absorption band near 820 nm), increased by the guiding effect.

The weak luminescence around 910 nm (10990 cm⁻¹), excited via the absorption near 820 nm (12195 cm⁻¹), is attributable to those transitions between the X₁ and A₂ states with absorption corresponding to the above transitions from vibrational states of X₁ to the ground vibrational state of A₂ and luminescence due to the 0–1, 0–2 and 0–3 transitions from the ground vibrational state of A₂ to excited vibrational states of X₁. Similarly, the weak luminescence near 830 nm (12050 cm⁻¹) excited via the absorption at about 760 nm (13155 cm⁻¹) is assignable to those transitions between the X₁ and A₂ states with absorption from the ground vibrational state of X₁ to excited vibrational states of A₂ (primarily, the 0–1, 0–2 and 0–3 transitions, with a vibrational frequency of 505 cm⁻¹ in the A₂ state [3, 5]) and luminescence due to the A₂ → X₁ transition described above.

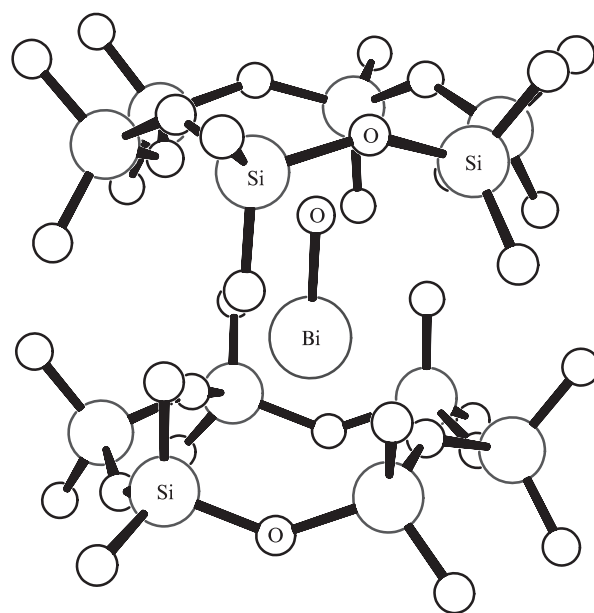
Thus, the assumption that the absorption and luminescence in bismuth-doped silica glass are due to transitions of interstitial BiO molecules fully accounts for the absorption/luminescence behaviour of this glass.

To verify whether interstitial BiO molecules can be present in the silica glass network, we performed quantum-chemical simulation using cluster models that considered one or two six-membered rings of SiO₄ tetrahedra. In the latter instance, the rings were coaxial and 3 Å apart. The dangling bonds of the oxygens on the cluster surface were saturated with hydrogen atoms. A BiO molecule was first placed in the centre position of the cluster, on the ring axis, and the cluster geometry was then fully optimised. All computations were performed with the GAMESS package [6] within the local-density-functional approach, using the BLYP functional, which is known to ensure good agreement between calculated and experimentally determined geometric parameters. We used the basis sets and effective core potentials proposed by Stevens et al. [7], with a *d*-polarisation function added to the basis sets of the oxygen and bismuth atoms (orbital exponents ζ_O = 0.800 bohr and

ζ_{Bi} = 0.185 bohr). For the hydrogen atoms, the standard 3-21G basis set was used.

According to analogous calculations performed earlier [8], a BiO molecule in aluminosilicate glass has no stable interstitial position: the molecule reacts with the surrounding atoms to give a threefold coordinated bismuth atom. In silica glass, however, a BiO molecule has an equilibrium interstitial position between six-membered rings of the SiO₂ network. In this position, the BiO molecule is oriented along the axis of the rings (Fig. 2). This configuration is stable: a deviation or displacement of the molecule from the axis does not lead to any reaction with its environment.

Simulation of the vibrational properties of a BiO molecule in ring interstices of the SiO₂ network has shown that the Bi–O stretching frequency is close to that in a free molecule (~700 cm⁻¹). This mode should be both IR active (absorption coefficient, ~1.6 D² amu⁻¹ Å⁻²) and Raman active (Raman activity, ~32 Å⁴ amu⁻¹; depolarisation ratio, 0.015). In addition, the interstitial BiO molecule has librational (395 and 430 cm⁻¹) and translational (60, 80 and 95 cm⁻¹) modes, but the corresponding IR absorption and Raman activity are too weak to be detected experimentally, all the more because of the low bismuth concentration in the glass.

**Figure 2.** BiO molecule in a ring interstice of the silica glass network (simulation results).

Based on the above, it is of interest to carry out the following experiments:

(1) to measure the lifetime of the states responsible for the luminescence near 1430 and 830 nm under excitation in the short-wavelength absorption band (below 450 nm), which would considerably reduce the reabsorption effect;

(2) to study Raman scattering in fibres with a bismuth-doped silica core in order to detect the stretching band of the BiO molecule;

(3) to measure the absorption and luminescence spectra of bismuth-doped silica with a high resolution at low temperatures (no higher than 20 K under the assumption that band broadening is primarily due the translational modes of interstitial BiO molecules) in order to reveal the vibrational structure of the absorption and luminescence bands; and

(4) to reproduce earlier experiments [1, 2] and perform the measurements listed above using bismuth-doped α -quartz crystals.

Such experiments would allow us to check the assumption that the IR luminescence of bismuth-doped silica glass is due to interstitial BiO molecules.

References

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