

Origin of broadband near-infrared luminescence in bismuth-doped glasses

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Interstitial negative-charged bismuth dimers, Bi_2^- and Bi_2^{2-} , are suggested as a model of broadband IR luminescence centers in bismuth-doped glasses. The model is based on quantum-chemical calculations of equilibrium configurations, absorption, luminescence, and luminescence excitation spectra of the dimers in an aluminosilicate network and is supported by IR luminescence observed for the first time, to our knowledge, in bismuth-doped polycrystalline magnesium cordierite. © 2008 Optical Society of America
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Broadband near-IR luminescence in the 1100–1400 nm range recently discovered in bismuth-doped glasses [1] has been observed in aluminosilicate, borate, phosphate, and chalcogenide bismuth-doped glasses (see the recent review [2], and references therein for details). Despite numerous observations of the IR luminescence, not only in bulk glass but in optical fibers as well [3,4], and its successful applications for lasing [5], the origin of the IR luminescence is not understood yet. Several models have been suggested (see [2]) based on electronic transitions in Bi^+ , Bi^{2+} , and Bi^{5+} ions, BiO interstitial molecules, and Bi clusters.

Recently an assumption has been made [6] that the IR luminescence is caused by electronic transitions in interstitial negatively charged Bi_2^- dimers. We have performed quantum-chemical calculations of spectroscopic properties of Bi_2^- and Bi_2^{2-} dimers and modeled these dimers in an aluminosilicate glass network.

Electronic states of Bi_2^- and Bi_2^{2-} dimers were calculated by the method of configuration interaction in active orbital space with spin-orbit interaction taken into account. The molecular wave functions were obtained by the density functional method in perturbation theory with multiconfigurational self-consistent-field reference functions. We used the GAMESS (US) quantum-chemical code [7], the Perdew–Burke–Ernzerhof functional, and Stevens–Basch–Krauss–Jasien–Cundari effective core potentials and bases [see the GAMESS (US) manual [7] for details] in the calculations. To test our approach we calculated the electronic spectrum of the BiO molecule and reproduced with good accuracy the results of a precision calculation [8].

Total energy curves for low-lying states of the Bi_2^- dimer are shown in Fig. 1. Optical absorption in bands near 860, 720, and 460 nm and ≤ 400 nm is caused by dipole-allowed transitions from the ${}^2\Pi_{1/2g}$ ground state to the ${}^2\Sigma_{1/2}$ excited ones. The IR luminescence arises owing to spin-forbidden transitions from the lowest excited quadruplet states, one ${}^4\Pi_{1/2}$ (1450 nm) and two ${}^4\Pi_{3/2}$ (1300 and 1050 nm). On the grounds of our calculations, lifetimes of these three quadruplet states are estimated to be of the order of

$10^3 \mu\text{s}$. Absorption in the 860 nm band can result in luminescence in the 1450 and 1300 nm bands, and absorption in the 720 and 460 nm bands can give rise to the luminescence in all three bands, 1450, 1300, and 1050 nm. In addition, excitation in the 720 nm band (and probably in the 460 nm band) leads to luminescence at 750 nm with a relatively short lifetime (estimated to be of the order of $10 \mu\text{s}$) that is due to the slightly allowed transition from the third excited ${}^2\Sigma_{1/2}$ doublet state to the ground state.

Total energy curves for low-lying states of the Bi_2^{2-} dimer are shown in Fig. 2. The ${}^3\Pi_{2g}$ triplet state turns out to be the ground state. Two more triplet states are found near the ground one, ${}^3\Pi_{1g}$ and ${}^3\Pi_{2g}$, with excitation energy of about 550 cm^{-1} . Allowed transitions from the ${}^3\Pi_{2g}$ ground state to ${}^3\Sigma$ excited states correspond to absorption bands near 880, 715, and 470 nm and ≤ 400 nm. The IR luminescence at 1420–1520, 1275–1375, and 1000–1060 nm is caused by spin-forbidden transitions from the three lowest ${}^1\Sigma$ singlet excited states to the ${}^3\Pi$ triplet ground

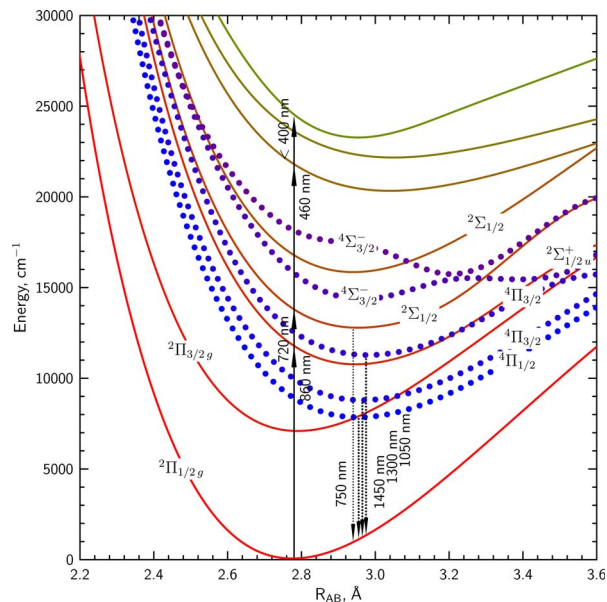


Fig. 1. (Color online) Low-lying states of Bi_2^- dimer.

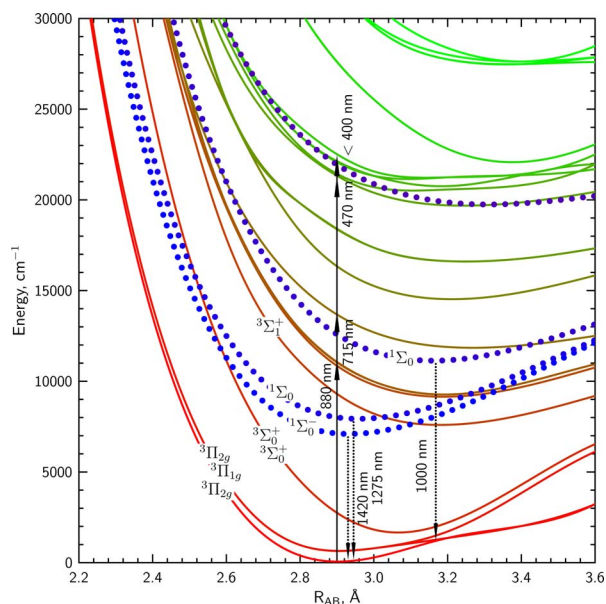


Fig. 2. (Color online) Low-lying states of Bi_2^{2-} dimer.

state or to one of the two first excited ${}^3\Pi$ triplet states. Again, lifetimes of these three singlet states are estimated to be of the order of $10^3 \mu\text{s}$, and absorption in the 880 nm band gives rise to IR luminescence in ~ 1470 and ~ 1325 nm bands, and absorption in 715 and 470 nm bands leads to luminescence in all three IR bands. However, now there is no luminescence near 750 nm.

So the calculated absorption and IR luminescence spectra of negatively charged Bi_2^- and Bi_2^{2-} dimers agree nicely with the experimental data available on the broadband IR luminescence in bismuth-doped glasses [1,2,6].

In a neutral host a negatively charged center is stable regarding dissociation with an electron released if $\mu^+ < 0$, where $\mu^+ = E(N+1) - E(N) - \epsilon_A$ is the so-called electric level of the center [9], $E(N)$ is formation energy of the center in the charge state with N electrons, and ϵ_A is electron affinity of the host. For silica glass $\epsilon_A \approx 0.9$ eV [10]. On the strength of our calculations with the host dielectric polarization taken into account, using the Onsager approach [7] with $\epsilon_{\text{SiO}_2} \approx 2.10$, the electric levels of the Bi_2^- and Bi_2^{2-} dimers are estimated to be $\mu_{\text{SiO}_2}^+ \approx -1.7$ eV and $\mu_{\text{SiO}_2}^+ \approx -0.2$ eV, respectively. Hence in silicate host with no free carriers the negatively charged Bi dimers, both Bi_2^- and Bi_2^{2-} , should be stable.

To verify these estimations we performed quantum-chemical modeling of Bi_2 , Bi_2^- , and Bi_2^{2-} dimers in aluminosilicate network, using a cluster approach. The clusters consisted of one or two six-member rings formed by four SiO_4 tetrahedra and two AlO_4 tetrahedra with dangling bonds of the outer O atoms saturated with H atoms. Two or four extra electrons were added into the clusters to ensure Al atoms to be fourfold coordinated. The bismuth dimer was placed initially in the center of the cluster, and the complete geometry optimization was performed. To model the negatively charged Bi_2^- and Bi_2^{2-} dimers, one or two more electrons were added to each cluster.

We used GAMESS (US) quantum-chemical code, the density functional method with a Becke–Lee–Yang–Parr functional and Stevens–Basch–Krauss–Jasien–Cundari bases, and effective core potentials with one d -type polarization function added for each O atom.

The neutral Bi_2 dimer in aluminosilicate glass network turned out to be aligned along the ring axis with Bi atoms on both sides of the ring plane. Both one and two extra electrons added into the cluster are found to be localized almost completely in Bi atoms forming just negative dimers, Bi_2^- or Bi_2^{2-} , respectively. The equilibrium configuration of Bi_2^- or Bi_2^{2-} dimer in the interstitial site formed by two six-member rings in aluminosilicate network is shown in Fig. 3. Bi atoms did not form a bond with any atom of the rings and returned to these positions even after the dimer was displaced considerably from the equilibrium configuration.

For negative bismuth dimers to be formed, free electrons must occur in the host. In aluminosilicate glasses threefold-coordinated O atoms may provide the electrons (see, e.g., [11]). Such O atoms do necessarily occur in an aluminosilicate network to ensure its continuity. Al atoms can be sixfold or fourfold coordinated. The sixfold-coordinated Al atoms cannot be built in a continuous silicate network as separate one-atom impurity centers: They must form groups containing not less than 4–6 Al atoms, and such groups can be bonded with silicate environment only with threefold-coordinated O atoms. So our model gives insight into the results of [12], where the bismuth-related IR luminescence was observed only in the presence of sixfold-coordinated Al atoms. In glasses containing oxides of alkaline or alkaline-earth elements free electrons are provided by positive ions of these elements.

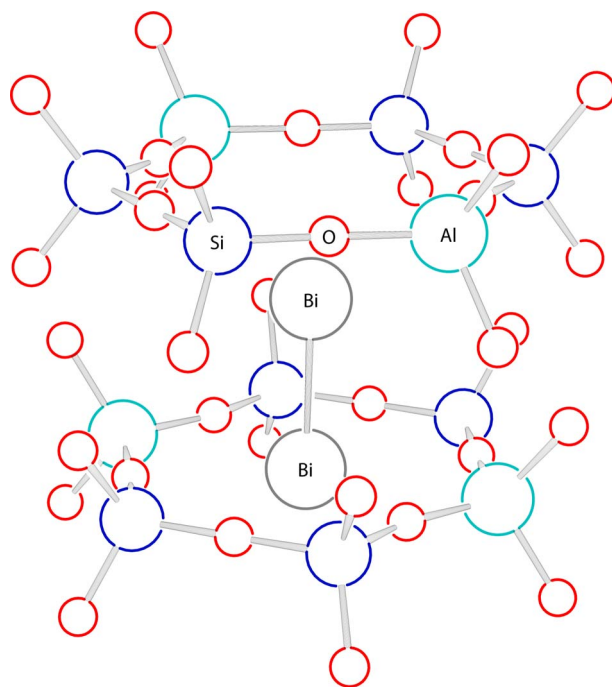


Fig. 3. (Color online) Bi_2 or Bi_2^{2-} dimer in an aluminosilicate network.

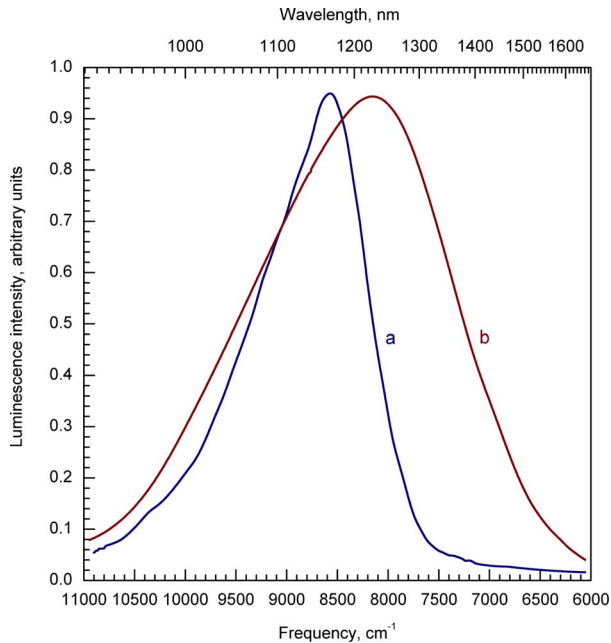


Fig. 4. (Color online) Room-temperature IR luminescence in bismuth-doped cordierite excited at (a) 514 nm, (b) 808 nm.

The single-charged Bi_2^- dimer has an unpaired electron and may be observed in electron spin resonance (ESR) spectra. An axial ESR signal with $g_{\parallel} \approx 2.20$ attributed just to the Bi_2^- dimer by analogy to Se_2^- was actually found in bismuth-doped glasses [6]. We calculated the ESR g factor of the Bi_2^- dimer with Dalton quantum-chemical code [13], using the same basis and effective core potentials, and found $g_{\parallel} \approx 2.1940$. On the other hand, the absence of any ESR signal caused by the IR luminescence center in bismuth-doped glasses was especially emphasized in [1]. This contradiction may be resolved under the assumption that the relation between Bi_2^{2-} and Bi_2^- dimers can change significantly depending on glass composition and manufacturing peculiarities since both dimers have similar spectra of IR luminescence and its excitation but Bi_2^{2-} dimers do not give rise to an ESR signal corresponding to spin 1/2.

To verify our model of the origin of IR luminescence in bismuth-doped aluminosilicate glasses we have studied luminescent properties of magnesium cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) containing about 2 at.% Bi. According to [14], in this crystal Bi atoms can occupy two crystallographic sites in the axis of interstitial channels formed by the six-member rings built of SiO_4 and AlO_4 tetrahedra. Two Bi atoms occupying adjacent sites can form Bi_2 dimers. As discussed above, these dimers should proceed to negative charge states, Bi_2^- or Bi_2^{2-} , capturing one or two electrons from the host. If this is the case, IR luminescence should be observed in bismuth-doped cordierite.

When the polycrystalline samples of bismuth-doped cordierite are excited by either 514 or 808 nm light, a broad IR luminescence band does actually arise in the expected wavelength range (Fig. 4).

In conclusion, we calculated electronic and optical spectra of Bi_2^- and Bi_2^{2-} negative dimers and equilibrium configuration of the dimers in aluminosilicate hosts. The results obtained confirmed assumptions made in [6] and allowed us to put forward a model of broadband IR luminescence in bismuth-doped glasses according to which interstitial negative bismuth dimers are the centers of the IR luminescence. Our calculation proved the negative bismuth dimers to be stable in aluminosilicate glass networks and proved their absorption, luminescence, and luminescence excitation spectra to be in close agreement with those observed in experiments.

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