Centers of near-IR luminescence in Bi-doped SiO_{2} and GeO_{2}: First-principle modeling and experimental data analysis

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First-principle study of possible bismuth-related centers in SiO_{2} and GeO_{2} hosts is performed and the results are compared with the experimental data. The following centers are modeled: trivalent and divalent Bi substitutional centers; BiO interstitial molecule; interstitial ion, Bi^{+}; Bi···≡Si – Si≡ and Bi···≡Ge – Ge≡ complexes formed by interstitial Bi atoms and glass intrinsic defects, ≡Si – Si≡ or ≡Ge – Ge≡ oxygen vacancies; interstitial dimers, Bi_{0}^{0} and Bi_{0}^{0}. Experimental data available on bismuth-related IR luminescence in SiO_{2}:Bi and GeO_{2}:Bi glasses, visible (red) luminescence in SiO_{2}:Bi glass and luminescence excitation are analyzed. A comparison of calculated spectral properties of bismuth-related centers with the experimental data shows that the IR luminescence in SiO_{2}:Bi and GeO_{2}:Bi is most likely caused by Bi···≡Si – Si≡ and Bi···≡Ge – Ge≡ complexes, and divalent Bi substitutional center is probably responsible for the red luminescence in SiO_{2}:Bi.

I. INTRODUCTION

Bismuth-doped glasses and optical fibers based on such glasses attract a considerable interest caused by characteristic broadband IR luminescence in the range from 1.0 up to 1.7 µm and even beyond, covering almost entire telecommunications window. Bismuth-doped glasses become a promising active medium. Such glasses and fibers are studied intensively and used successfully in fiber amplification and lasing (see e.g. the reviews [8–10]). The origin of IR luminescence centers is still not clear. However for the last few years an opinion has received a recognition that the luminescence is very likely caused by subvalent Bi centers [8] (see [12] as well). In particular, monovalent Bi centers are of special interest.

In understanding the origin of the luminescence centers simple hosts are of a specific interest since those allow one to get more unambiguous data in both experimental and theoretical studies. For example, such simple crystals as halides of monovalent metals, are convenient [9, 10]. As for fiber optics applications, in this regard the results of investigation of the luminescence in optical fibers with bismuth-doped silica (SiO_{2}) and germania (GeO_{2}) glass core not containing any other dopants [7–12] are undoubtedly of a prime importance. The main results concerning the spectral properties of SiO_{2}:Bi are confirmed later independently (see e.g. Refs. [13, 14]). For further analysis the following spectral properties of bismuth-related centers in SiO_{2}:Bi and GeO_{2}:Bi discovered in Refs. [7,14] seem to be of a principal interest:

i. luminescence around 1.43 µm is excited in SiO_{2}:Bi by absorption near 1.43, 0.83, 0.42, 0.37 and 0.24 µm [8,10,14];

ii. luminescence around 1.67 µm is excited in GeO_{2}:Bi due to absorption near 1.65, 0.93, 0.46 and 0.40 µm [9,10,12];

iii. luminescence near 0.83 µm is excited in SiO_{2}:Bi by absorption near 0.83 and 0.42 µm [9];

iv. luminescence near 0.95 µm is excited in GeO_{2}:Bi by absorption near 0.93 and 0.46 µm [9];

v. luminescence in the red range, 0.60–0.65 µm, is excited in SiO_{2}:Bi due to absorption near 0.48, 0.37 and ≲0.29 µm [9,14]; no such luminescence is observed in GeO_{2}:Bi [9];

vi. an electron-hole recombination excitation mechanism contributes to the red luminescence, but not to the IR one in SiO_{2}:Bi under intensive UV illumination [14];

vii. red luminescence in SiO_{2}:Bi is thermally quenched at temperatures ≳450 K, while the IR luminescence is not quenched up to the temperature of 700 K [10,14];

viii. the lifetimes of the states responsible for the luminescence near 1.43 and 0.83 µm in SiO_{2}:Bi and near 1.67 µm in GeO_{2}:Bi, are 640, 40 and 500 μs, respectively [8,12] (no data available on lifetime of the state responsible for 0.95 µm luminescence in GeO_{2}:Bi).

Qualitative similarity of the absorption and luminescence spectra in SiO_{2}:Bi and in GeO_{2}:Bi should be particularly emphasized. In Refs. [7,12], where this fact was revealed, the suggestion was made that the centers responsible for the IR luminescence in bismuth-doped SiO_{2} and GeO_{2} glasses have a common origin and a similar
In the present work we report the results of computer modeling of possible bismuth-related centers in bismuth-doped SiO$_2$ and GeO$_2$ glasses and try to interpret the above-listed experimental data.

II. MODELING OF BISMUTH-RELATED CENTERS

The modeling of bismuth-related centers in silica and germania glass network was performed using periodical network models. $2 \times 2 \times 2$ and $3 \times 3 \times 2$ supercells of SiO$_2$ and GeO$_2$ lattices of $\alpha$ quartz polymorph structure were chosen as initial models of perfect networks. The supercells contained, respectively, 24 or 54 SiO$_2$ (GeO$_2$) groups (72 or 162 atoms). Using ab initio Car-Parrinello molecular dynamics the system formed by supercells was heated to temperature as high as 2000 K (SiO$_2$) or 1500 K (GeO$_2$), maintained at this temperature until the equilibrium atom velocities distribution was reached and then cooled to 300 K. Periodical models of SiO$_2$ and GeO$_2$ networks based on final supercell configurations were applied to study the bismuth-related centers. Bi atoms (e.g., an interstitial atom) were placed in the central region of the supercell. As well an oxygen vacancy, $\equiv$Si–Si$\equiv$ or $\equiv$Ge–Ge$\equiv$, was formed there by a removal of one of the O atoms. Charged centers were simulated changing the total number of electrons in the supercell. Equilibrium configurations of Bi centers were found by a subsequent Car-Parrinello MD and complete optimization of the supercell parameters and atomic positions by the gradient method.

All calculations of SiO$_2$ and GeO$_2$ network models and configuration of bismuth-related centers were performed using Quantum-Espresso package in the plane wave basis in generalized gradient approximation of density functional theory with ultra-soft PAW pseudopotentials. The pseudopotential sources were taken from library v. 0.3.0 pseudopotential library. PBE density functional was used both in building the pseudopotentials and in calculations. To test the approach, SiO$_2$ and GeO$_2$ lattice parameters were calculated for $\alpha$ quartz unit cell and for supercells with both atomic positions and cell parameters completely optimized. The convergence was tested with respect to the plane wave cutoff energy and the $k$ points grid choice. The energy cutoff $\geq 950$ eV and the number of $k$ points $\geq 64$ in the irreducible part of unit cell Brillouin zone were found to be enough to converge the total energy within $10^{-3}$ eV per atom and to reproduce the experimental lattice parameters with a relative accuracy of $\leq 5 \times 10^{-3}$. The geometry of supercells was reproduced with a relative accuracy better than $2 \times 10^{-2}$ with only $\Gamma$ point of the supercell taken into account and better than $1 \times 10^{-3}$ using $8 \times 8 \times 8$ $k$ points in the supercell in irreducible part of the supercell Brillouin zone. The total energy convergence was not worse than that in case of the unit cell.

Configurations of bismuth-related centers obtained by this means were used to calculate the electron localization functions using the programs from Quantum-Espresso package, to calculate and analyze the electron density distribution and effective charges of atoms by Bader’s method (bader v. 0.28 code), and to calculate the absorption spectra of the centers by Bethe-Salpeter equation method based on all-electron full-potential linearized augmented-plane wave approach. The latter calculations were performed with Elk code in the local spin density approximation with PW-CA functional. Spin-orbit interaction essential for Bi-containing systems was taken into account. Scissor correction was used to calculate transition energies. The scissor value was found basing on calculations with modified Becke-Johnson exchange-correlation potential known to yield accurate band gaps in wide-band-gap insulators, sp semiconductors, and transition metal oxides. The non-overlapping mufﬁn-tin (MT) spheres of maximal possible radii $R_{\text{MT}}$ were used. Convergence of the results was tested with respect to plane-wave cutoff energy, the angular momentum cutoff for the MT density and potential, and the $k$ points grid choice. The plane-wave cutoff, $k_{\text{max}}$, was determined by $R_{\text{MT}}^\text{min} \cdot k_{\text{max}} = 7$ relation with $R_{\text{MT}}^\text{min}$, being the smallest MT radius. The angular momentum cut-off was taken to be $l = 10$. The self-consistent calculations were performed on $4 \times 4 \times 4$ grid of $k$ points uniformly distributed in irreducible part of the supercell Brillouin zone. Further increasing the cutoff and $k$ points density did not change the results significantly. The total energy self-consistence tolerance was taken to be $10^{-3}$ eV per atom. More dense $k$ points grid, $8 \times 8 \times 8$, was used to calculate dipole matrix elements for optical spectra.

Configurational coordinate curves of bismuth-related centers were calculated in a simple model restricted to the lowest excited states basing on absorption spectra dependence on Bi atom(s) displacement along three mutual orthogonal directions. In spite of the fact that the model is inherently approximate, it shows that in all Bi interstitial-related centers under consideration the Stokes shift corresponding to a transition between the first excited state and the ground one do not exceed the accuracy of the excited state energy calculation. Hence it is reasonable enough to estimate the IR luminescence wavelengths in such centers by taking the Stokes shift to be zero. On the contrary, in all centers with oxygen-bonded Bi atom(s) the corresponding Stokes shift turns out to be large. So in such centers we can estimate only roughly the IR luminescence wavelengths by analogy with known centers in other hosts.

In our approach only approximate calculations of absorption intensities or excited states lifetimes are possible. Much higher density of the $k$ points grid and, in general, a considerably larger supercell are required to achieve an accuracy comparable to the experimental data. Nevertheless, a comparison of the results of
test calculations performed in our approach and the experimental data available for exciton absorption in SiO$_2$ and for =Si oxygen-deficient center absorption in silica glass showed that the relative absorption intensity is reproduced with an accuracy not worse than an order of magnitude. In view of the above remark about the excited states one might expect that the relative lifetimes of the states responsible for the luminescence are estimated with nearly the same accuracy.

III. RESULTS OF CALCULATIONS ON BISMUTH-RELATED CENTERS IN SiO$_2$ AND GEO$_2$ HOSTS

Basing on the assumptions concerning subvalent Bi states we studied several bismuth-related centers in SiO$_2$:Bi and GeO$_2$:Bi networks, as follows:

— trivalent Bi substitutional center;
— divalent Bi substitutional center;
— BiO interstitial molecule;
— interstitial single-changed ion, Bi$^+$, and interstitial atom, Bi$^{00}$;
— Bi···≡Si−Si≡ and Bi···≡Ge−Ge≡ complexes formed by interstitial Bi atom and glass intrinsic defect, ≡Si−Si≡ or ≡Ge−Ge≡ oxygen vacancy;
— interstitial Bi dimers, Bi$^{00}$ and Bi$_2^-$.

These centers correspond to different bismuth oxidation levels (valence states), namely, Bi$^{III}$ (trivalent Bi substitutional center), Bi$^{II}$ (divalent Bi substitutional center and BiO molecule), Bi$^I$ (interstitial single-changed ion, Bi$^+$, and Bi···≡Si−Si≡ or Bi···≡Ge−Ge≡ complexes), and to completely reduced Bi (interstitial atom, Bi$^{00}$, and Bi$^{00}$ and Bi$_2^-$ dimers). We believe that our choice covers sufficiently wide range of the most probable bismuth-related centers in SiO$_2$:Bi and GeO$_2$:Bi glasses.

A. Trivalent Bi substitutional center

According to our modeling of Bi substitutional centers in SiO$_2$ and GeO$_2$ networks, Bi atoms occupying, respectively, Si or Ge sites, can form substitutional centers of two types, threefold coordinated Bi atoms bonded by three bridging O atoms with Si (Ge) atoms, and fourfold coordinated Bi atoms in bi-pyramidal configuration bonded by four bridging O atoms with Si (Ge) atoms. In addition to bridging O atoms, in both cases there are also O atoms completing the Bi atoms coordination to fivefold or sixfold ones. These O atoms interact slightly with Bi atoms forming only very weak bonds. Threefold (to be more specific, 3 + 3- or 3 + 2-fold) coordination of atoms is typical of trivalent Bi compounds and of impurity bismuth centers in many hosts (see e.g. [28][29]).

Fourfold (4 + 2- or 4 + 1-fold) coordination of Bi atoms is known to occur in some crystalline bismuth compounds (see e.g. [30][31]). Formation of additional bonds of Bi atom in such centers becomes possible owing to threefold coordinated O atom occurring anywhere in the network. Four-coordinated Bi atoms turn out to be rather unstable: in the modeling they are either easily transformed into threefold coordinated atoms or even not formed at all.

In the centers with threefold coordinated Bi atoms the Bi−O distances are found to be approximately 0.213 nm for three bridging O atoms and 0.34 − 0.36 nm for complementary O atoms. The angles between Bi−O bonds are about 94.6° for bridging O atoms. In the centers with fourfold coordinated Bi atoms the Bi−O distances are approximately 0.209 and 0.230 nm for equatorial and axial bridging O atoms, respectively, and about 0.33 nm for complementary O atoms. The O−Bi−O valence angles are about 92.2° and 160.8° for equatorial and axial bridging O atoms, respectively. Spectral properties of trivalent substitutional Bi centers (usually named as Bi$^{3+}$ impurity centers) are much studied (see e.g. [28][29]). Absorption and luminescence bands corresponding to $^3$S$_0 \leftrightarrow ^3$P$_1$ transition in Bi$^{3+}$ ion are commonly observed [32][34]. Sometimes the absorption corresponding to the $^1$S$_0 \rightarrow ^1$P$_1$ transition is present as well. Wavelengths of absorption and luminescence bands are subject to wide variations depending on the host: luminescence in the 0.28–0.55 µm range is excited by absorption in the 0.23–0.33 µm range. Lifetimes of excited states
responsible for the luminescence are typically of 1–5 µs in different hosts. The results of our modeling suggest that these variations may be explained by a prevailing coordination of trivalent Bi. E.g. in SiO\textsubscript{2} the most intensive absorption band of the threefold coordinated Bi atom is found to be near 0.26 µm but the same band of the fourfold coordinated Bi atom turns out to be shifted to 0.22 µm. In GeO\textsubscript{2} the absorption bands of threefold and fourfold coordinated Bi atoms occur near 0.24 and 0.23 µm, respectively. Stokes shift turn out to be large in all these cases. Hence we can do no more than suggest, by analogy with the experimental data available [28, 29], that the luminescence in the 0.3–0.4 µm range may be excited in the above-mentioned absorption bands.

**B. Divalent Bi substitutional center**

The modeling revealed that in SiO\textsubscript{2} network the divalent bismuth forms twofold coordinated Bi atoms bonded by bridging O atoms bonded by bridging O atoms with Si atoms. In GeO\textsubscript{2} such twofold coordinated Bi atom does not occur since GeO\textsubscript{2} network readily transforms resulting in a formation of threefold coordinated Bi atom (the above-described trivalent substitutional center), sixfold coordinated Ge atom, and threefold coordinated O atom.

Calculation of electron density distribution by Bader’s method proves the effective charge of twofold coordinated Bi atom to be +1.316 e. The effective charges of bridging O atoms bonding Bi atom with Si ones turn out to
be \(-1.629\) e, and those of Si atoms are +3.927 e. In perfect SiO\(_2\) network the effective charges of O and Si atoms calculated using the same approach are found to be \(-1.965\) e and +3.930 e, respectively. Hence an extra charge as large as \(\approx +1.99\) e turns out to be localized in Bi atom and bridging O atoms, suggesting that Bi atom is divalent in this center. In Fig. 1 the distribution of electron density around twofold coordinated Bi atom is shown. One can recognize two Bi−O bonds formed.

Calculated energy levels and transitions in Bi\(^{2+}\) substitutional center (Fig. 2) agree well both with the data available on absorption and luminescence of divalent Bi centers \([35–37]\) and with the spectra measured in fibers and fiber preforms with SiO\(_2\) core \([9] [14]\). The ground state of free Bi\(^{2+}\) ion is known to be \(^2P_{1/2}\) and the first excited state with the energy about 20800 cm\(^{-1}\) is \(^2P_{3/2}\) \([32] [34] [38]\). In crystal field this excited state is split in two sub-levels, \(^2P_{3/2}(1)\) and \(^2P_{3/2}(2)\). According to Refs. \([33] [37]\), the absorption bands characteristic of Bi\(^{2+}\) correspond to \(^2P_{1/2} \rightarrow \rightarrow ^2P_{3/2}(1)\), \(^2P_{1/2} \rightarrow \rightarrow ^2P_{3/2}(2)\), and \(^2P_{1/2} \rightarrow \rightarrow ^2S_{1/2}\) transitions. Luminescence in 0.55–0.65 \(\mu\)m range (in different hosts) excited in these absorption bands corresponds to \(^2P_{3/2}(1) \rightarrow \rightarrow ^2P_{1/2}\) transition. In our calculation the absorption bands corresponding to three above-mentioned transitions are near 0.52, 0.37, and < 300 \(\mu\)m, respectively (Fig. 2(a)). As in the case of trivalent Bi centers, Stokes shift turns out to be large in divalent Bi substitutional center, and so we can estimate only the luminescence wavelength as 0.6–0.7 \(\mu\)m, by analogy with the data of Refs. \([35] [37]\).

### C. Interstitial BiO molecule

We have found in our modeling that in SiO\(_2\) network there is an equilibrium position of BiO molecule in the interstitial site formed by six-member rings of SiO\(_4\) tetrahedra. In such a position the BiO molecule is placed between two neighboring rings being aligned along the interstitial axis. This position of BiO molecule is found to be quite stable: being forcedly declined from the interstitial axis or shifted aside, the molecule do not enter into reaction with the surrounding atoms and returns to the initial position. The present modeling confirms the results of our previous calculation (see Fig. 2 in Ref. \([39]\) performed in a cluster model of SiO\(_2\) network using quantum-chemical methods. This is very distinct from the case of aluminosilicate glasses \([40]\), where the interstitial position of BiO molecule turns out to be completely unstable, and BiO molecule reacts readily with neighboring atoms forming threefold coordinated Bi atom.

In contrast to SiO\(_2\), interstitial BiO molecule is not found to occur in GeO\(_2\) network in our modeling. Quite as it is in aluminosilicate host, the molecule reacts with GeO\(_2\) network with threefold coordinated Bi atom formed.

Spectral properties of BiO molecule are well under-

![FIG. 3. Total energy curves and transitions in BiO molecule according to data of Refs. \([41] [43]\).](image)

stood \([41] [43]\). Total energy curves of BiO molecule obtained from the configuration interaction calculations with spin-orbit interaction taken into account \([41]\) and corrected to achieve more close agreement with the experimental data \([42] [43]\) are given together with possible transitions in Fig. 3 (see as well Fig. 1 in Ref. \([39]\)).

### D. Interstitial Bi\(^{0}\) atom and Bi\(^{+}\) ion

According to the calculations, both Bi\(^{0}\) atom and Bi\(^{+}\) ion can occur as interstitial centers in six-member ring interstitial sites both in SiO\(_2\) and GeO\(_2\) hosts (Fig. 4). The Bi interstitial atom or ion turn out to interact weakly with the surrounding atoms and, as may be seen from Fig. 4, do not form any bond with them. This means that the influence of the host on electronic states and spectral properties of interstitial Bi atom and ion consists mainly in crystal field effect.

So the spectral properties of the interstitials may be understood in a model similar to the theory of Tl\(^{3+}\)(1) center \([41]\). A weak axial crystal field is caused by O and Si ions of SiO\(_4\) six-member rings surrounding the interstitial center.

Three lowest states of Bi\(^{+}\) ion are known to arise from \(^3P\) atomic state split by a strong spin-orbital interaction \([32] [34] [38]\). The ground state of Bi\(^{+}\) ion, \(^3P_0\), is not split by the crystal field. The first excited state, \(^3P_1\), is split by an axial crystal field in two levels (approximately 10100 and 12300 cm\(^{-1}\) in SiO\(_2\) and 10100 and 11400 cm\(^{-1}\) in GeO\(_2\)), and the second excited state, \(^3P_2\), is split in three
FIG. 4. Calculated electron density maps of the centers formed by Bi interstitials: (a) Bi\(^0\) atom in SiO\(_2\), (b) Bi\(^0\) atom in GeO\(_2\), (c) Bi\(^+\) ion in SiO\(_2\), (d) Bi\(^+\) ion in GeO\(_2\). The map plane goes through Bi atom and two nearest O atoms in each case.

levels (approximately 15500, 16600 and 20800 cm\(^{-1}\) in SiO\(_2\) and 13500, 15400 and 18000 cm\(^{-1}\) in GeO\(_2\)), as displayed in Figs. 2(b) and 2(c), respectively. Electric dipole transitions between three spin-orbital components of \(^3\)P state forbidden in a free Bi\(^+\) ion become allowed due to state mixing under the influence of the crystal field. Levels and transitions schemes of Bi\(^+\) interstitial ions in SiO\(_2\) and GeO\(_2\) are given in Figs. 2(b) and 2(c), respectively.

The ground state of Bi\(^0\) atom, \(^4\)S\(_{3/2}\), and the first, \(^2\)D\(_{3/2}\), and second, \(^2\)D\(_{5/2}\), excited states are split by the axial crystal field. The third excited state, \(^2\)P\(_{1/2}\), cannot
be split by the electrostatic field. Electric dipole transitions from the ground state of Bi\(^0\) interstitial to all the states arising from \(^2\)D atomic state, turn out to be weak since in a free atom such transitions are parity-forbidden. Hence the only relatively intensive absorption band corresponding to \(^4\)S\(_{3/2} \rightarrow ^2\)P\(_{1/2}\) transition is expected to occur in Bi\(^0\) center, in the \(\lesssim 0.4\ \mu\)m range, as follows from our calculations.

E. Complexes formed by interstitial Bi atom and oxygen vacancy

According to our calculations, interstitial Bi atoms, Bi\(^0\), can form complexes with intrinsic defects, \(\equiv\text{Si} - \text{Si}\equiv\) or \(\equiv\text{Ge} - \text{Ge}\equiv\) oxygen vacancies, in SiO\(_2\):Bi and in GeO\(_2\):Bi, respectively.

We modeled oxygen vacancies, \(\equiv\text{Si} - \text{Si}\equiv\) in SiO\(_2\) and \(\equiv\text{Ge} - \text{Ge}\equiv\) in GeO\(_2\), using the same models and calculation approach as described above. In single \(\equiv\text{Si} - \text{Si}\equiv\) vacancy the distance between Si atoms is found to be 0.244 nm, and in single \(\equiv\text{Ge} - \text{Ge}\equiv\) vacancy the distance between Ge atoms is 0.258 nm. In both vacancies a covalent bond between Si or Ge atoms is formed, somewhat relaxed in comparison with crystalline Si or Ge. When a complex is formed with interstitial Bi atom, the distance between Si atoms in \(\equiv\text{Si} - \text{Si}\equiv\) vacancy increases to 0.381 nm, and the distance between Ge atoms in \(\equiv\text{Ge} - \text{Ge}\equiv\) vacancy increases to 0.391 nm. The distances between the Bi atom and Si (Ge) atoms turn out to be 0.254 and 0.262 nm, respectively. Bader’s analysis of electron density proves the effective charge of Bi atom to be +0.511 e\(^-\) and +0.616 e\(^-\) in SiO\(_2\):Bi and GeO\(_2\):Bi, respectively. Effective charges of Si (Ge) atoms in the vacancy are found to be +3.020 e\(^-\) and +1.661 e\(^-\), respectively. In single \(\equiv\text{Si} - \text{Si}\equiv\) and \(\equiv\text{Ge} - \text{Ge}\equiv\) vacancies the effective charges of Si and Ge atoms calculated using the same approach are +3.006 e\(^-\) and +1.863 e\(^-\), respectively. So an extra charge \(\approx +0.46\) e\(^-\) and \(\approx -0.98\) e\(^-\) is transferred from Bi and Si (Ge) atoms into the area between these Bi and Si (Ge) atoms and, to a lesser extent, into the area between two Si (Ge) atoms.

Corresponding electron density distributions are shown in Figs. 5(a) and 5(b) in Si–Bi–Si and Ge–Bi–Ge planes. Thus, three-center mutually bound group of Bi atom and two Si (Ge) atoms is formed instead of a pair of covalently bonded Si (Ge) atoms. Coordination-type three-center bond would be expected to occur in such a complex. It can be seen in Figs. 5(a) and 5(b) that Bi atoms remains substantially isolated and do not form pronounced two-center bonds with Si or Ge atoms.

Levels and transitions schemes of Bi···\(\equiv\text{Si} - \text{Si}\equiv\) and Bi···\(\equiv\text{Ge} - \text{Ge}\equiv\) complexes in SiO\(_2\):Bi and GeO\(_2\):Bi are...
shown in Figs. 2(d) and 2(e), respectively.

Again, the spectral properties of such a complex may be understood in a crystal-field model. Basing on the described rearrangement of the electron density, one may consider the complex in a rough approximation as a pair of centers, an interstitial Bi$^+$ ion and a negatively charged $\equiv$Si$^-$Si$\equiv \equiv$Ge$^-\equiv$Ge$\equiv$ vacancy, similar to thallium and lead centers in crystalline alkali and alkali-earth halides (see e.g. discussion in [4]) or to a complex formed by bismuth substitutional center and anion vacancy in TlCl crystal [5, 6]. In other words, the center is considered to be a Bi$^+$ ion in axial crystal field formed by a neighboring negatively changed oxygen vacancy. The ground state of Bi$^+$ ion, $3P_0$, is not split. The first excited state, $3P_1$, is split by axial crystal field in two levels, approximately 7000 and 7900 cm$^{-1}$ in SiO$_2$ and 5900 and 6600 cm$^{-1}$ in GeO$_2$. The second excited state, $3P_2$, is split in three levels, approximately 11000, 12200, and 24400 cm$^{-1}$ in SiO$_2$ and 9500, 10500, and 22600 cm$^{-1}$ in GeO$_2$. The next excited state of Bi$^+$ ion, $1D_2$, is split in three levels as well, energy of the lowest of those being about 27000–28000 cm$^{-1}$ and other two lie at 41000–45000 cm$^{-1}$. One more excited state of Bi$^+$ ion, $1S_0$, not split by the crystal field, occurs somewhat above 45000 cm$^{-1}$ in SiO$_2$ or 46000 cm$^{-1}$ in GeO$_2$ (Fig. 2 (d) and [c]). Electric dipole transitions between the ground state and the split excited ones become allowed due to state mixing in the crystal field.

It should be realized that whilst such a model is useful to understand qualitatively the origin of IR luminescence in Bi···≡Si$^-$Si$\equiv$ and Bi···≡Ge$^-\equiv$Ge$\equiv$ complexes, it nevertheless provides only very approximate description of their electronic structure. In fact, changes in electronic states and spectral properties of Bi ion in Bi···≡Si$^-$Si$\equiv$ and Bi···≡Ge$^-\equiv$Ge$\equiv$ complexes go far beyond the crystal field effect in comparison with both free Bi$^+$ ion and the above-considered interstitial Bi$^+$ ion. The coordination-bond-type distribution of electron density covers both the Bi atom and two Si (Ge) atoms in the oxygen vacancy. This results in Bi ion states split and mixed considerably stronger than it is even possible in the crystal field (e.g., in the case of interstitial Bi$^+$ ions). As a result, the corresponding transition wavelengths turn out to be increased considerably. In GeO$_2$ the electron density redistribution is more pronounced, and transitions in Bi···≡Ge$^-\equiv$Ge$\equiv$ center turn out to be shifted to larger wavelengths than in Bi···≡Si$^-$Si$\equiv$ one. On the other hand, since no distinct diatomic covalent bonds, Bi–Si or Bi–Ge, are formed in the complexes, the electronic states of Bi···≡Si$^-$Si$\equiv$ and Bi···≡Ge$^-\equiv$Ge$\equiv$ centers turn out to depend very slightly on small displacements of Bi atom. Hence Stokes shift is expected to be low, at least for the most long-wave transitions.

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FIG. 6. Total energy curves and transitions in Bi$_2^-$ dimer

F. Interstitial Bi dimers

The modeling proves both neutral, Bi$_2^0$, and negative single-charged, Bi$_2^-$, bismuth dimers to occur in SiO$_2$ network in stable positions in interstitial sites formed by six-member rings of SiO$_4$ tetrahedra. Similar to BiO molecule discussed above, Bi$_2^0$ or Bi$_2^-$ dimer lie in such equilibrium positions between two adjacent rings being aligned along the ring interstitial axis. Again, either forced declination from the axis or shift aside do not lead to any reaction of the dimer with the surrounding atoms. Recently such stable positions of Bi dimers were found in aluminosilicate glasses in our calculations performed by quantum-chemical methods in cluster models of the networks [40]. On the contrary, only neutral interstitial dimer, Bi$_2^0$, is found to be stable in GeO$_2$ network. The negatively charged dimer, Bi$_2^-$, turns out to be unstable, and once placed into the ring interstitial site, readily enters into reaction with the neighboring atoms. As a result, three- and fourfold coordinated Bi atoms (in other words, trivalent Bi substitutional centers discussed in Section IIIA) are formed.

Spectral properties of Bi$_2^-$ dimer have been studied in enough detail, for the first time in Ref. [15] and later in Refs. [10, 46], by configuration interaction method in various approximations. The calculated total energy curves for several low-lying states of Bi$_2^-$ dimer are shown in Fig. 6 (see as well Fig. 3 in [15], Fig. 1 in [40], and Fig. 1 in [46]). Transitions and corresponding absorption and possible luminescence in Bi$_2^-$ dimers are discussed in detail in Refs. [40, 46].
FIG. 7. Comparison of the calculated levels and transitions schemes of centers formed by Bi interstitial atom and oxygen vacancy with the empirical schemes of bismuth-related centers in SiO$_2$ and GeO$_2$ suggested in Refs. [9][11]: (a) Bi$^0$ and $\equiv$Si–Si$\equiv$ vacancy in SiO$_2$ vs. Si-BAC center; (b) Bi$^0$ and $\equiv$Ge–Ge$\equiv$ vacancy in GeO$_2$ vs. Ge-BAC center. Level energies are given in $10^3$ cm$^{-1}$, transition wavelengths in $\mu$m.
### IV. DISCUSSION

Comparing the experimental data reported in Refs. [8–12, 13] (see Section I) with the above-described results of our calculations, one may safely suggest that the bismuth-related centers giving rise to IR luminescence in SiO$_2$:Bi and GeO$_2$:Bi glasses are likely to be, respectively, Bi···≡Si−Si≡ and Bi···≡Ge−Ge≡ complexes formed by interstitial Bi atoms and oxygen vacancies. Indeed, the calculated spectral properties of these complexes are in good agreement with the experimental data [1–3] (page 1). According to the calculations, in SiO$_2$:Bi bismuth-related absorption is expected in two broad bands near 1.4 and 0.8 µm, and in two bands near 0.4 and 0.35 µm. Broad-band near-IR luminescence near 1.4 µm is expected to be excited in all these absorption bands, and the IR luminescence in the 0.8–0.9 µm range is expected to be excited in the latter three absorption bands. In GeO$_2$:Bi bismuth-related absorption is expected in broad bands near 1.6 and 1.0 µm, and in the bands near 0.45 and 0.3 µm. Near-IR luminescence in a broad band near 1.6 µm is expected to be excited in all these absorption bands, and the IR luminescence in the 0.9–1.0 µm range is expected to be excited in the latter three absorption bands. As evident from all these data displayed in Fig. 7, the calculated levels and transitions schemes of Bi···≡Si−Si≡ and Bi···≡Ge−Ge≡ centers accord closely with the empirical schemes proposed in Refs. [9,11]. As well the suggested model of bismuth-related centers provides a support for the above-mentioned hypothesis concerning a common origin and similar structure of near-IR luminescence centers in bismuth-doped SiO$_2$ and GeO$_2$ glasses [7,12].

On the other hand, interstitial BiO molecules and interstitial negatively charged Bi$_2^-$ dimers could contribute to IR luminescence in SiO$_2$:Bi as well. Spectral properties of BiO molecule were discussed in detail in Ref. [39] specifically in relation to interstitial BiO molecule in SiO$_2$ glass, and were shown to agree well with the experimental absorption and luminescence spectra observed in SiO$_2$:Bi [7,9]. In general, spectral properties of Bi$_2^-$ dimer agree satisfactorily with these experimental spectra [40,46], with two additional remarks: the luminescence corresponding to the transition near 1.300 µm might not be observed in experiment due to low excitation efficiency, and the absorption and luminescence in the 0.82–0.83 µm range may be ascribed to the transitions near 0.72 µm and near 0.86 µm, respectively (see Fig. 6 and Figures 1 in Refs. [10,16]). However, according to our modeling, neither interstitial BiO molecules nor interstitial negatively charged Bi$_2^-$ dimers can occur in GeO$_2$:Bi. Thus, among all the bismuth-related centers studied, Bi···≡Si−Si≡ and Bi···≡Ge−Ge≡ complexes seem to be the most appropriate model of IR luminescence bismuth-related centers of the same origin both in SiO$_2$ and GeO$_2$.

In general, the results of our modeling support the suggestions concerning the origin of red luminescence in SiO$_2$:Bi glasses made in Refs. [8,9,14], and allow one to understand the absence of such luminescence in GeO$_2$:Bi glasses. However it seems reasonable to discuss certain suggestions [14] in more detail.

According to Ref. [14], there are luminescence centers of two types in SiO$_2$:Bi. Bi centers of the first type are responsible for IR luminescence near 1.4 µm with a long lifetime excited only by intra-center absorption. Centers of the second type give rise to red luminescence near 0.63 µm with a short lifetime excited not only by intra-center absorption but by electron-hole recombination as well. Such centers trap electrons excited to the conduction band by two-photon absorption of intense UV laser light, and the recombination of trapped electrons with holes gives rise to red luminescence. The centers responsible for IR luminescence are not quenched up to the temperature of 700 K, but the red luminescence centers are thermally quenched at temperatures $\gtrsim$ 450 K [13] in page 1. Such different properties of bismuth-related centers might be explained by the fact that the first-type center weakly interacts with the glass network and, as a result, it is temperature-resistant and cannot capture conductive electrons and participate in the process of electron-hole recombination excitation of the luminescence. The second-type center is embedded in the glass network and hence it is subject to temperature quenching and is able to capture conductive electrons with subsequent excitation of red luminescence owing to electron-hole recombination.

The results of modeling bismuth-related centers described in Sections IIIB and IIIE allow an understanding the assumptions made by the authors of Ref. [14] on the basis of their experimental data. Indeed, if the IR luminescence center in SiO$_2$:Bi is a complex of interstitial Bi atom and SiO$_2$ intrinsic defect,

| Table I. Estimated relative lifetimes of luminescence in bismuth-related centers |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Bi$^{3+}$       | Bi$^{2+}$       | BiO             | Bi··· vacancy    |
|                 | Bi··· ≡Si−Si≡   | Bi··· ≡Ge−Ge≡   | Bi··· ≡Si−Si≡   |
| near-IR         | $\gtrsim 10^2$  | $\gtrsim 10^2$  | $\gtrsim 10^2$  | $\gtrsim 10^2$  |
| visible / IR    | $\sim 10$      | $\gtrsim 10$    | $\gtrsim 10$    | $\sim 10$      | $\sim 10$      |


\[ \equiv \text{Si} - \equiv \text{Si} \equiv \] oxygen vacancy, its thermal stability should be only somewhat lower than the stability of the vacancy, since in such a complex the Bi atom forms only weak bonds with the glass network. Further, these bonds are formed with Si atoms of the vacancy, but not with O atoms. This eliminates the possibility of recombination of an electron trapped in such a center with a hole in the glass valence band, since in SiO\(_2\) the states near the upper edge of the valence band are formed mainly by non-bonding 2p electron states (lone pairs) of bridging O atoms. On the other hand, if the red luminescence center is the glass valence band, since in SiO\(_2\) of an electron trapped in such a center with a hole in the Bi atom covalently bonded with two bridging O atoms, the thermal stability of such a center should be considerably lower than the stability of the vacancy owing to low coordination of the Bi atom. The bridging O atoms in this center allow effective recombination of a hole with a trapped electron.

To realize the possibility of conduction electron to be captured in the defects under consideration we calculated electron affinities of Bi···≡Si—Si≡ complex and of Bi\(^{2+}\) substitutional center using the approach developed in Ref. [47]. The electron affinity is found to be approximately of 2.1 and 4.2 eV for these centers, respectively. According to different estimations [15–50], electron affinity of vitreous SiO\(_2\) host is known to be from 0.9 to 2.7 eV. Hence our calculations suggest that conduction electron can be readily trapped in divalent Bi substitutional center, Bi\(^{2+}\), and can hardly be trapped in Bi···≡Si—Si≡ center. This is in obvious agreement with the assumptions made in Ref. [14].

As noted above, comparing the results of lifetime calculations with the experimental data on the excited states responsible for the luminescence in SiO\(_2\):Bi and GeO\(_2\):Bi [11] in page 1 is meaningful only by an order of magnitude. For this purpose the calculated relative lifetimes are listed in Table 1 with the lifetime corresponding to the most intensive transition in Bi\(^{2+}\) substitutional center (the absorption near 0.25 \(\mu\)m, the luminescence in the 0.3–0.4 \(\mu\)m range, see Section [II A] taken to be unity. The lifetime of corresponding luminescence of trivalent Bi in different hosts is known to be 1–5 \(\mu\)s [28, 29].

Using this estimation together with the data given in Table 1 one can easily see that the results of lifetime calculations agree satisfactorily with the experimental data both for IR luminescence of Bi···≡Si—Si≡ and Bi···≡Ge—Ge≡ centers and red luminescence of Bi\(^{2+}\) substitutional center.

V. CONCLUSION

Basing on the results of our modeling of bismuth-related centers in SiO\(_2\):Bi and GeO\(_2\):Bi glasses and taking into account the assumption concerning common origin of Bi centers responsible for IR luminescence in silica and germania glasses, it may be safely suggested that the bismuth-related centers of near-IR luminescence in SiO\(_2\):Bi and GeO\(_2\):Bi glasses are mainly represented by the Bi···≡Si—Si≡ and Bi···≡Ge—Ge≡ complexes formed by interstitial Bi atoms and intrinsic defects of glass, ≡Si—Si≡ and ≡Ge—Ge≡ oxygen vacancies. Interstitial BiO molecules and negatively charged Bi\(_2\) dimers might also contribute to the IR luminescence in SiO\(_2\):Bi glass as well but are absent in GeO\(_2\) host. Bismuth-related centers responsible for the visible (red) luminescence in the SiO\(_2\):Bi glass are likely to be represented by twofold coordinated Bi atoms bonded with Si atoms by bridging O atoms.

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