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综 合 评 述

铋(Bi)：赋予光纤光子技术光学材料“神奇”特性的奇异金属

ELOPOV Alexander, RIUMKIN Konstantin, KHEGAI Aleksandr, ALYSHEV Sergey, FIRSTOV Sergei

(俄罗斯科学院普罗霍罗夫普通物理研究所 季亚诺夫光纤研究中心，莫斯科 119333，俄罗斯)

摘　要：高速通信技术的飞速发展，现已实现 4K 视频直播、远程实时手术、人工智能、物联网、虚拟现实、云服务及社交媒体的广泛应用。数字技术的进一步发展，无疑需要光纤通信领域的创新性解决方案，这一需求的核心驱动力是对更高传输速率的迫切追求。多波段波长传输技术被视为实现该目标的最具潜力途径之一，该技术可充分利用标准单模光纤中从 O 波段到 U 波段的全波段低损耗区间，使光通信系统的带宽提升数倍。掺铋光纤凭借其优异的增益特性与噪声系数表现，成为光放大器的独特介质，是多波段传输技术成功落地的核心器件。尽管掺铋材料的研发已历经 20 余年，但其相关研究热度仍持续攀升。本文综述阐述了掺铋光学材料（涵盖晶体、陶瓷、玻璃及光纤）新型结构的研发现状与趋势，同时介绍了这类材料的创新制备方法；分析了提升掺铋材料性能的独特技术路径，展示了不同光谱波段下掺铋光纤放大器的代表性研究成果，并归纳了其他研究团队的重要发现。

关键词：光学材料；光纤；陶瓷；玻璃；铋；发光特性；放大器；激光器
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1　Introduction

In 2025, nearly 25 years have passed since the first observation of near-IR (NIR) luminescence in bismuth-doped glasses and 20 years since the development of the first Bi-doped fiber laser[1–2]. The optical properties of Bi-doped materials are remarkably diverse, as demonstrated by their ability to produce broad luminescence spanning from the UV to the NIR region. To date, no other chemical element has been found to exhibit such a wide range of emission. This unique behavior might even lead one to wonder if bismuth has “magical” properties. The modern starting point for this field is often considered to be a paper by Fujimoto *et al.* who reported the observation of long-lived IR luminescence in Bi-doped aluminosilicate glasses [3], although earlier works on Bi-containing materials with IR emission bands also exist[4]. Initial interest in such optical media was driven by the fact that they showed bright luminescence in spectral regions unreachable by traditional rare-earth- doped oxide glasses. Subsequent progress, from fundamental experiments to the development of commercially viable fiber-optic amplifiers, has been significant. This advancement was made possible through a series of scientific breakthroughs in the field of bismuth-doped optical fibers, which revealed their extraordinary characteristics. Systematic research into the optical properties of glasses with different chemical compositions, as well as detailed studies of their spectral and luminescence properties, made it possible to identify a number of types of bismuth active centers (BACs) with optical transitions in the NIR. Moreover, a major step forward came with the classification of BACs and the determination of their relationship with the structural and physico-chemical parameters of the glass matrix[5–6]. It is now well established that there are four primary types of BACs associated with Si, P, Al and Ge atoms. Their characteristic luminescence bands of these BACs are

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第一作者：ELOPOV Alexander(1995—)，男，博士研究生。
通信作者：FIRSTOV Sergei(1984—)，男，教授。

Received date: 2025–08–29.　**Revised date:** 2025–11–13.
First author: ELOPOV Alexander(1995–), male, Doctoral candidate.
E-mail: saelopov@yandex.ru
Correspondent author: FIRSTOV Sergei(1984–), male, Professor.
E-mail: fir@fo.gpi.ru

shown in Fig.1. An important outcome of decades-of research has been the development of a family of bismuth-doped fibers for use in novel photonic devices capable of lasing and amplifying optical radiation from 1.15 to 1.78 μm. Bismuth-doped fiber lasers can be used as wavelength converters, transforming the output of other single-mode lasers, or operate as brightness amplifiers. Comprehensive reviews provide detailed information on such lasers[7–8]. Additionally, the development of pulsed laser systems based on Bi-doped fibers has enabled significant practical applications in fields such as optical tomography, remote sensing, and medical procedures[9–11]. While most laser experiments have utilized optical fibers, other types of bismuth-doped materials—such as crystals, bulk glasses, and glass-ceramics—remain underexplored and are the subject of ongoing research. Therefore, this review will consider not only the achievements related to Bi-doped fibers, but also the results of research on other types of bismuth-containing materials. Despite significant progress in understanding the physical nature of BACs there are still various hypotheses about their structure. This includes Bi^{5+} [3,12–13], Bi^{+} [14–16] to Bi_2, Bi_2^{-}, Bi_2^{2-} [17–20], Bi^0 [21], BiO species [22–24], and point defects[25–27], the detailed structure and features of these materials remain the subject of ongoing discussion [28]. This paper will present some recent original results that contribute to this discussion. In the final section, we will discuss significant recent developments in bismuth-doped fiber amplifiers and their key performance parameters that make these amplifiers highly promising for future high-capacity communication systems.

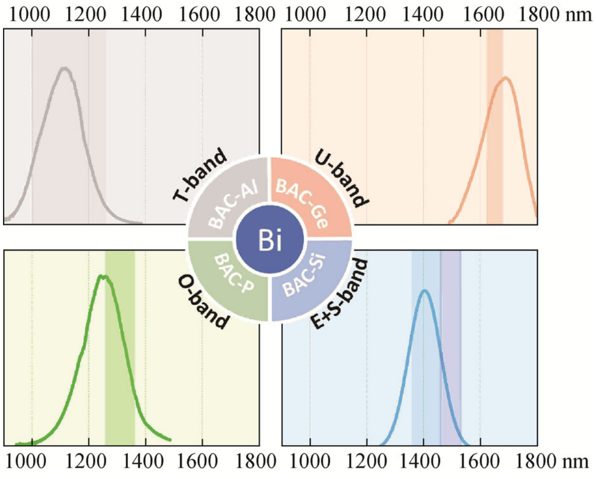


Fig. 1 Characteristic emission bands attributed to various types of BACs

2 Bismuth-doped optical materials for NIR region

It is well known that bismuth, unlike ions of rare earth elements, has a fundamentally different structure of the electron shell (Xe) $4f^{14}$ $5d^{10}$ $6s^2$ $6p^3$, where the outer 6s and 6p shells are filled with valence electrons. As a result, the electron-phonon interaction and the symmetry of the local environment can have a significant impact on the optical properties of bismuth ions when embedded in glass and crystal structure. This circumstance explains the observed dependence of the luminescent and absorbing properties of BACs on the chemical composition and local environment. Below, we will summarize information about the features of BACs in various structures.

2.1 Crystals and ceramics

Over the past twenty years, numerous Bi-doped crystals have been studied that cannot all be covered in this review. Therefore, we will focus on some of the most characteristic aspects. In general, crystals have several advantages over glasses for laser applications, including narrower luminescence bands, higher quantum yield, and higher absorption cross-sections. In Bi-containing crystals, IR luminescence with a long lifetime (2 μs to 1000 μs) can be observed in various spectral regions, ranging from 700 nm to 1700 nm[29]. Many of the studied crystals exhibit ultra-broadband luminescence, for example, $Ba_3Sc_4O_9$ emits in the wavelength region of 1.1–1.7 μm with a peak near 1.3 μm[30]. However, such broad bands are not typical of highly-ordered structures. The study of Bi-doped crystalline media has been motivated not only by the desire to obtain record-wide IR luminescence but also by the ability to stabilize a specific valence state of bismuth and conduct a wide range of experiments with unambiguous results. The valence of a bismuth ion in the crystal lattice usually corresponds to the valence of the substituted ion (isomorphic substitution), which is fundamentally different from what occurs in glass, where “valence” electron may be delocalized and the valence state is intermediate. Although the stabilization of Bi^0 and Bi^+ ions at the Ba^{2+} site has been demonstrated[31–33], numerous studies suggest the possibility of isomorphic substitution to stabilize bismuth ions in a specific valence state with optical transitions in the NIR. In particular, the selection of a specific host crystal, as mentioned above, allowed for the isomorphic substitution of large cations with comparable size (such as K^+, Rb^+, Cs^+, Tl^+, Ba^{2+}) with Bi^+ (the ionic radius of the crystal cation is ~ 1.52 Å). The first crystal of this type, $RbPb_2Cl_5$ doped with bismuth, was grown and studied in 2008[34]. The main results concerning the optical properties of the studied bismuth-doped crystals, including the aforementioned type, are presented in Table 1.

Table 1 Main characteristics of Bi-doped crystals

Compound	Crystal	Substitution ion	$\lambda_{em}/\lambda_{exc}$/nm	Proposed active center	Lifetime/μs	Year	Ref.
Fluoride	BaF_2	Ba^{2+}	900–1600/540	Bi^{2+}, Bi^+	2.5, 2.1	2009	[40]
	PbF_2	Pb^{2+}	900–1650/600	Bi^+	4.7, 6.5	2018	[41]
	SrF_2	Sr^{2+}	800–1400/700	Bi^{2+}, Bi^+	25	2016	[39]
Chloride	$Ba_5(PO_4)_3Cl$	Ba^{2+}	1000–1600/690	Bi^+		2013	[35]
	$Ba_{10}(PO_4)_6Cl_2$	Ba^{2+}	950–1550/690	Bi^+		2012	[42]
	AgCl	Ag^+	700–1300/420	Bi^+	10.3	2013	[43]
	TlCl	Tl^+	950–1600/410	Bi^+	200–350	2013	[44]
	$CsCdCl_3$	Cs^+	800–1200/615	Bi^+	360	2014	[45]
	RbY_2Cl_7	Rb^+	900–1200/660	Bi^+	469	2016	[46]
	$KAlCl_4$	K^+	825–1150/600	Bi^+	525	2012	[47]
	$KMgCl_3$	K^+	800–1150/600	Bi^+	400	2013	[48]
	$Ba_2B_5O_9Cl$	Ba^{2+}	800–1500/300–670	Bi^0	30.19	2012	[49]
	$RbPb_2Cl_5$	Pb^{2+}	900–1300/808	Bi^+, Bi^{2+}	140	2008	[34]
	$RbAlCl_4$	Rb^+	800–1150/600	Bi^+	520	2016	[50]
	$CsAlCl_4$	Cs^+	800–1150/600	Bi^+	455	2016	[50]
	$RbMgCl_3$	Rb^+	800–1100/600	Bi^+	436	2016	[50]
	$CsMgCl_3$	Cs^+	800–1100/600	Bi^+	385	2016	[50]
	$KCdCl_3$	K^+	850–1150/600	Bi^+	280	2016	[50]
	$RbCdCl_3$	Rb^+	850–1150/600	Bi^+	374	2016	[50]
Bromide	$CsCdBr_3$	Cs^{2+}	1050/530–690	Bi^+	250	2015	[51]
Iodide	CsI	Cs^+	1000–1700/808	Bi^+, Bi-cluster	130, 220	2011	[52]
	$TlCdI_3$	Tl^+	900–1450/405–820	Bi^{2+}	30	2017	[53]
	$CsPbI_3$		1100–1300/360–470	Polaronic defect		2016	[54]
Borate	$\alpha-BaB_2O_4$	Ba^{2+}	1050–1500/808	Bi^+	526	2009	[36]
	SrB_4O_7	Sr^{2+}	1000–1500/808	$Bi^{<3+}$	>600	2009	[55]
Silicate	$KGaSi_2O_6$	K^+	950–1500/470, 532	Bi^+	400	2015	[56]
Aluminate	$Gd_{0.1}Y_{0.9}AlO_3$	Y^{3+}	900–1700/640–670	Bi^+		2018	[57]
	$XAl_{12}O_{19}$	Al^{3+}	650–850/330	Bi^{3+}	2.60–3.02	2020	[58]
Aluminosilicate	$KAlSi_2O_6$	K^+	1000–1600/470, 532	Bi^+	400	2015	[56]
	$CsAlSi_2O_6$	Cs^+	900–1400/405–690	Bi^+	400	2015	[56]
Phosphate	$Ba_2P_2O_7$	Ba^{2+}	950–1300/732	Bi^0	634	2010	[31]
	$BaBPO_5$	P^{5+}, B^{3+}	950–1600/476	$[BiO_x]$	81–116	2016	[59]
Tungstate	$PbWO_4$		950–1100, 1300–1450/940	Bi^+		2012	[60]
Germanate	Y_4GeO_8	Y^{3+}	900–1500/808	Bi^+		2011	[38]
	$CsGaGe_2O_6$	Cs^+	1000–1600/445–820	Bi^+		2019	[61]

It is important to emphasize that bismuth-doped crystals often do not exhibit IR luminescence. This statement is especially true for single-crystal samples, even when there is isomorphic substitution. To obtain IR emission, it is necessary to employ additional methods, both during the growth process[35] and afterward—such as heat treatment in a specific atmosphere or irradiation with high-energy radiation[36–39]. These methods are required not only for the stabilization of IR-active centers but also for ions with luminescence in the visible region. For example, in SrB_4O_7 single crystals, bismuth stabilizes mainly as Bi^{2+} ions, which exhibit intense orange luminescence; however, after heat treatment in a N_2 atmosphere, these ions show different characteristic properties[62–63]. An important aspect of growing bismuth-doped crystals is ensuring that the melt is sufficiently acidic to stabilize subvalent forms of Bi (namely Bi^+). This can be achieved by controlling the high oxoacidity of the melt in oxide crystals[64] or by ensuring a high proportion of Lewis acid halides in halide crystals. In addition, it is crucial to maintain optimal redox conditions during melt crystallization as in a highly oxidizing environment, subvalent bismuth can be oxidized to its stable +3 state, whereas excessive reduction converts bismuth into a black metallic colloid.

As demonstrated in several studies (*e.g.*, in Ref.[55]) it is often possible to form IR emitting centers only in polycrystals and glass-ceramics. This is likely due to the disruption of the highly ordered structure and symmetry of the crystalline phase, or to the absence of specific defects near the active Bi ion. In this context, the breaking of symmetry and the presence of additional grain boundaries act as favorable factors for the formation of these active centers. It should be noted that the boundary regions between such grains have a strong influence on the various properties of polycrystals. In these regions, the structure of the material can be quite different from that of a perfect crystal. This is supported by the results of studies on glass ceramics with nanoscale crystalline inclusions. These inclusions significantly alter the materials' spectral and luminescent properties[65]. Further evidence comes from the observation that the width of the luminescence and absorption bands in these materials is on the order of tens of nanometers, which is not typical of single-crystalline systems, as noted previously (Fig. 2).

Based on the data presented, it can be stated with confidence that is IR luminescence in these materials is associated with subvalent states of bismuth (Bi^+ and Bi^0). However, the precise relationship between the structure and properties is still unclear. There is evidence for a multicenter effect in crystals[66]. A comparison of the ionic radii of possible dimers (Bi_2, Bi_2^-, Bi_2^{2-}) with those of the host cations they would substitute shows that the incorporation of such dimers into regular lattice sites is unlikely. The presence of more than one type of center, which strongly depends on the type and structure of host material, has led numerous experimental studies and various theoretical interpretations in research on both crystalline and glassy materials, as will be discussed in the following section.

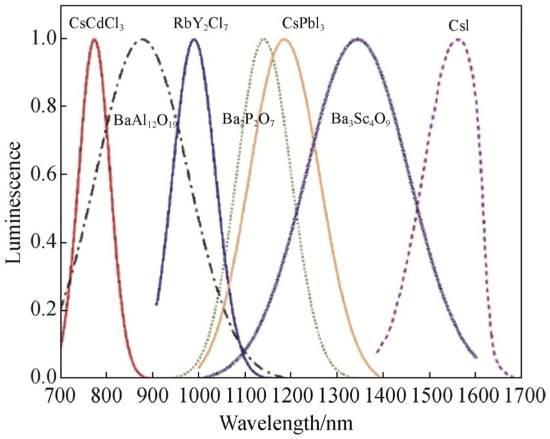


Fig. 2　Emission spectra of the studied Bi-doped crystals: $CsCdCl_3$ [45], $BaAl_{12}O_{19}$ [58], RbY_2Cl_7 [51], $Ba_2P_2O_7$ [31], $CsPbI_3$ [54], $Ba_3Sc_4O_9$ [30], CsI [52]

2.2　Bulk glasses

After the discovery of the first bismuth-activated glasses demonstrating broadband luminescence, numerous of papers have been published in this field, which presented the results of a wide range of studies on glasses with various chemical compositions based on oxides such as: SiO_2 (*e.g.*, [67–70]), P_2O_5 (*e.g.*,[71–73,15]); a mixture of GeO_2-SiO_2 (*e.g.*, [74]), B_2O_3 (*e.g.*, [14,71]) and GeO_2 (*e.g.*, [75–76]). The main goal of creating bulk glasses doped with bismuth was to create a laser-active medium in the IR spectrum. However, despite the efforts, no laser emission was achieved from bulk glasses over the past two decades. This is due to the poor amplifying properties of bulk glasses, which are associated with the use of high concentrations of Bi. This leads, on the one hand, to a significant change in the structure and optical properties of the active centers, including multicenter effects. On the other hand, in combination with slow cooling of the glass, it results in high unsaturable losses. Both factors negatively impact the achievement of net optical gain in such materials, as opposed to the “on–off” gain that has been repeatedly demonstrated. Despite this, research on bulk materials continues, as their potential benefits are likely not yet exhausted. However, there has been a noticeable shift in the goals and focus of such research.

Much of the research on bulk glasses containing bismuth involves developing new methods and approaches based on chemical and coordination engineering. These approaches aim to effectively control the local environment of Bi, thereby altering its properties in a controlled manner[77], or to create additional sites for the effective formation of luminescent centers, influencing the characteristics of the glass network[78–79].

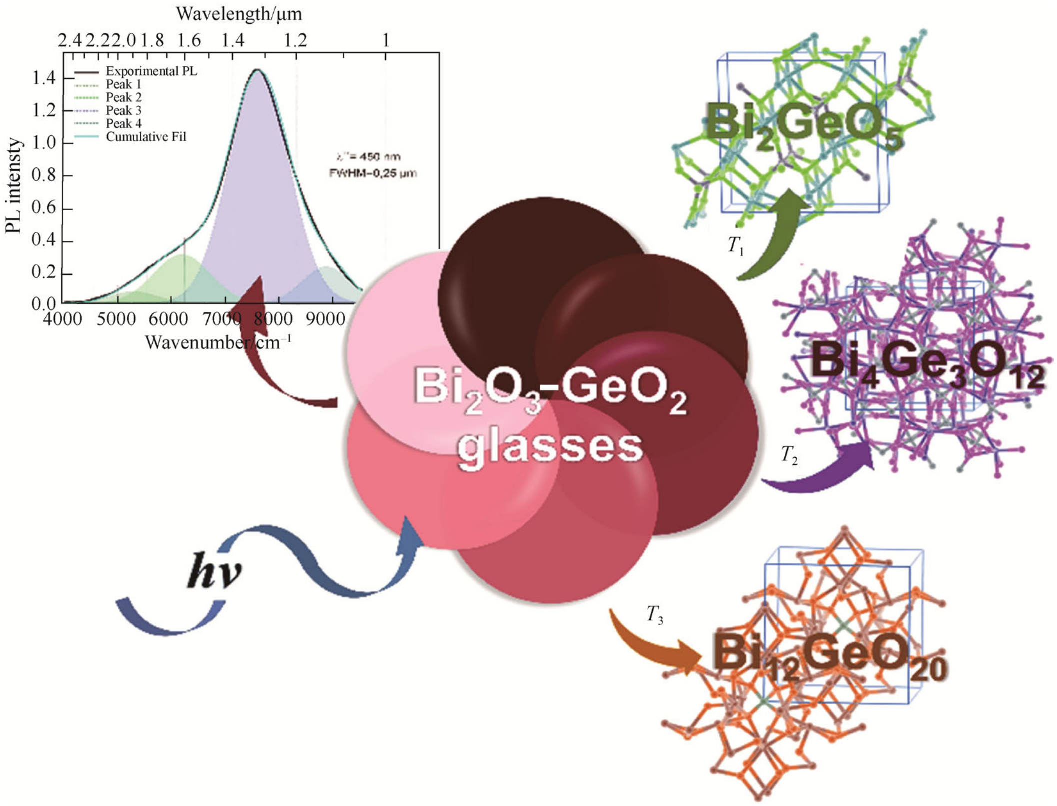


Fig. 3 Photoluminescence spectrum of $5Bi_2O_3$-$95GeO_2$ glass excited at 450 nm. The various crystalline phases, which can be formed in the bismuth-germanate glass, are demonstrated

The approach of modifying the coordination environment of bismuth ions is a direct and effective strategy, as it directly influences their luminescent properties, often leading to improved performance. An alternative method, which involves modulating the short- and medium-range topological order of the glass by controlling the Al_2O_3 content in a nitrided germanate glass doped with Bi, has also been explored[80]. This approach has enabled the achievement of wide IR luminescence bands with enhanced intensity. It was found that this effect resulted from an increased concentration of NIR emitting centers due to the combined addition of Si_3N_4 and Al_2O_3. The authors suggested that this behavior was caused by the reduction of Bi ions within the glass network structure, which remained unchanged despite the increased Al_2O_3 content. This implied that there was no change in the coordination of aluminum coordination incorporated into the glass network that provides favorable conditions for the formation of the NIR emitting centers. In addition, research continues on the development and study of optical glass-ceramics based on bismuth-doped germanosilicate glasses (Fig. 3)[81]. Thus, it can be argued that interest in germanate glasses has significantly increased recently. This may be due to the fact that this host matrix is favorable for the formation of BACs with characteristic emission bands centered at 1.35 μm and 1.65 μm, *i.e.* near the corresponding emission bands of Er-doped glass. These BAC emission bands can be combined to provide wideband amplification. It should be noted that the aforementioned approaches can be used effectively not only to modify and transform the properties of BACs, and address issues related to clustering effects. A strategy for controlling clusters in Bi-doped glasses and fibers with a broadband optical response was proposed in paper[82]. Zhang *et al.* demonstrated that the chemical state of the Bi centers—such as dispersed clusters, aggregated clusters, and isolated ions—can be controlled by modifying the glass with alkali ions. The addition of alkali ions to the glass network is believed to promote the breaking of bonds between [SiO_4] or [GeO_4] tetrahedra, leading to the formation of a more porous network structure, where dispersed Bi clusters can migrate more freely. With this approach, in glasses with high Bi_2O_3 content, the disruption of the glass network structure also affects the clustered forms of bismuth, reducing their number (Fig. 4).

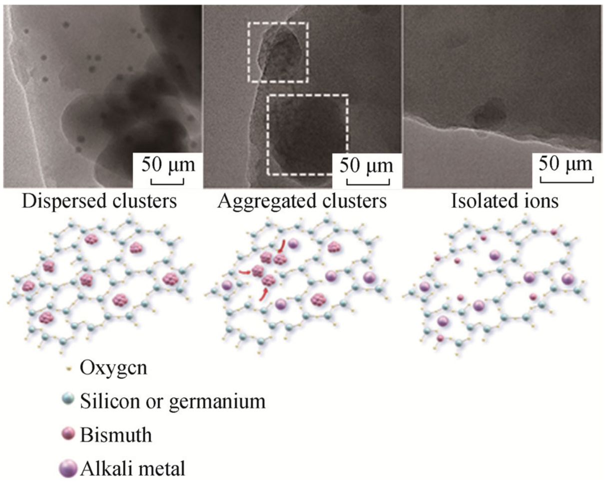


Fig. 4　Schematic diagram of the cluster control strategy: high-resolved transmission electron microscopy images of various forms of Bi in germanosilicate glass matrix

Another approach to improving the properties of bulk Bi-doped glasses, aimed at reducing clustering effects, is based on utilizing nanocage structures within porous silica glass. The first studies on bismuth doping using this method were carried out by Zhou *et al.*[83]. Significant interest in this approach stems from the development of high-purity nanoporous materials suitable for the development of fiber lasers[84]. The advantage of this approach is in uniform distribution of nanopores that can effectively disperse dopant ions and prevent clustering. Simple immersion techniques allow dopant ions to be uniformly embedded into the glass matrix. Furthermore, active fibers based on nanoporous silica glass exhibit a highly uniform refractive index and excellent optical homogeneity. Experiments with such glasses have demonstrated IR luminescence bands[85]. However, a detailed analysis to assess the advantages of these glasses compared to other methods has yet to be conducted.

It is certainly worth noting several interesting results from the creation and detailed study of bismuth-containing glasses using novel methods. A series of bismuth-activated germanosilicate glasses prepared by the sol-gel method combined with high-temperature sintering was studied. Interestingly, this approach allows for the formation of BAC-Ge and BAC-Si with typical absorption and luminescence bands even at high Bi concentrations (up to 10%, in mole). Previously, such results were unattainable using conventional processes. Another original method for producing multi-component glasses activated with Bi is mentioned in[86]. This new technique, termed “melt-in-melt”, involves a key step where one molten material is poured into another under continuous stirring at high temperature. This process enables the synthesis of glasses with an arbitrary SiO_2/P_2O_5 ratio, which is not feasible with conventional melt-quenching methods. Due to the nearly unlimited possibilities for developing new glass compositions, there is also a correspondingly high degree of freedom in the topological design of the glass structure, which, in turn, significantly affects the luminescent properties of active dopants. This approach is believed to mitigate the effect of bismuth clustering. Therefore, it can be concluded that the field of creating bismuth-doped glasses is still actively developing, with new approaches emerging that could be used in the future to improve the optical properties of the resulting glasses. It is important to emphasize that the focus of research on bismuth-containing materials has shifted toward the production of optical fibers. This is evidenced by the fact that in most studies on bismuth-activated glasses, the final step is to fabricate optical fibers made of the prepared glasses, typically using the “rod-in-tube” method. Fig. 5 shows a typical schematic diagram of the rod-in-tube drawing process, along with a photograph of the resulting preform and drawn fiber. The optical properties of such fibers are not yet comparable to those of fibers obtained by the conventional method of chemical vapor deposition (MCVD), which will be discussed in the next section.

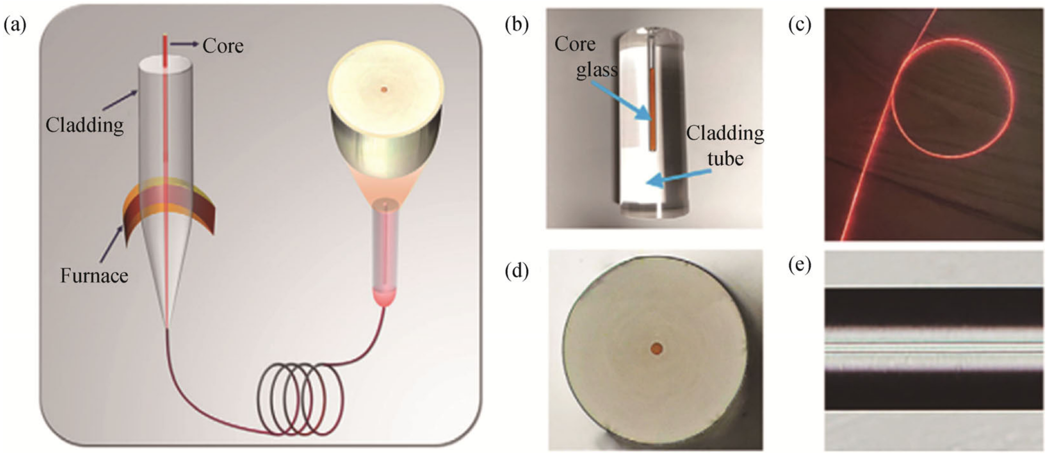


Fig. 5 (a) Schematic diagram of the drawing process by the rod-in-tube approach; (b) The photo of optical fiber preform; (c) Visible light transmission by the fabricated fiber; (d, e) Optical microscope images of the fiber cross-section and side section[87]

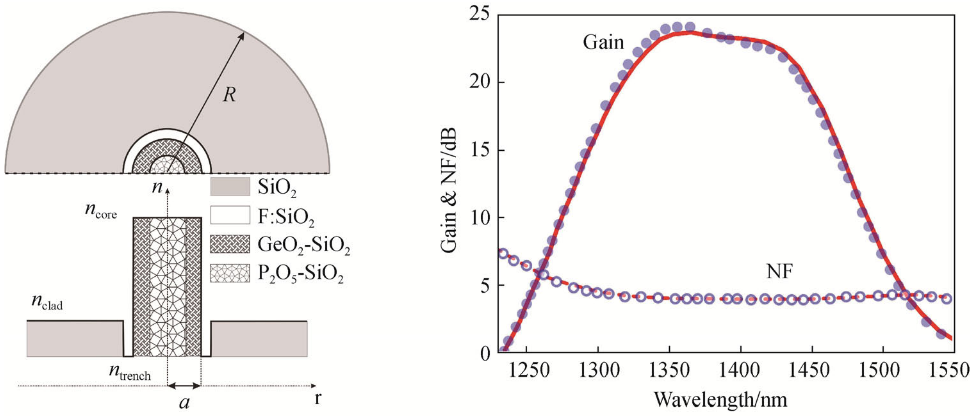
2.3 Bismuth-doped silica-based fibers with “magic” properties

Optical fibers are the only active medium that contain bismuth ions and can provide effective optical amplification over almost the entire wavelength range from 1.1 μm to 1.8 μm. Such fibers are fabricated from glass preforms obtained using the MCVD process[88]. Recently, there has been an increased attention to the study of bismuth-doped optical fibers due to their potential for developing advanced devices that are of great practical importance in next-generation telecommunications. A series of recent review papers has been published on the optical properties of bismuth-doped optical fibers and the devices based on them [89–94], reflecting the significant progress that has been made over the past two decades.

Bismuth-doped fibers exhibit unique properties, providing the ability to generate and amplify optical radiation in various NIR bands. When discussing the advantages of these optical fibers over other glassy materials, it is important to note the specific conditions of their production process. The drawing process makes favorable conditions form frozen (unrelaxed) glass states, which help in creation of BACs and prevent clustering effects that are difficult to overcome in bulk glasses[95–96]. The majority of research on bismuth-based optical fibers is aimed at practical applications, such as the development of stable and reliable fiber-optic amplifiers. In the following sections of this review, we will discuss different types of bismuth-doped fiber amplifiers that have been developed to date[97-101]. In these works, the main focus is on improving the gain spectrum by utilizing different types of BACs, particularly within the O + E + S band range.

However, the advantages of bismuth-doped fibers have been achieved through the use of scientific approaches. For example, as shown in[102], the smart confined doping of Bi allows for the control of the Bi→BAC conversion efficiency, leading to improved conversion rates of up to 30%, whereas for conventional fibers this parameter is about an order of magnitude lower. This has been achieved through the special forming the radial distribution of active (Bi atoms) and inactive (Ge atoms) dopants in the fiber core. This has reduced the number of Bi-related forms that contribute to unsaturable losses, which has had a positive effect on the laser efficiency. In addition, this approach has allowed the achievement of a record slope efficiency of 80% with respect to the launched pump power among existing Bi-doped fiber lasers.

Recently, a new efficient approach has been proposed to control the concentration of different types of BACs in a fiber core, enabling the effective achievement of a balanced BAC ratio, which is crucial for expanding the gain spectrum. This method is based on forming a fiber with a heterogeneous core structure[103–104]. Fig. 6a demonstrates the concept of such a Bi-doped fiber and the output characteristics of an amplifier based on it. Using this approach, each type of BAC forms within a favorable glass matrix that provides optimal performance parameters, as shown in Fig. 6b.



(a) (b)

Fig. 6 (a) Illustration of the concept of a heterogeneous-glass core Bi-doped fiber; (b) gain and noise figure (NF) of 808-nm-cladding-pumped amplifier developed based on heterogeneous-glass core Bi-doped fiber[103]

Another important result obtained recently was the development of a fiber with a high concentration of Bi, which has promising amplification characteristics. This was made possible through the effective optimization and control of a number of technological parameters that affect the formation of BACs and the centers responsible for the unsaturable losses. Thus, a net gain exceeding 45 dB was demonstrated in the wavelength range of 1.41–1.43 μm using a 12-meter-long optical fiber [105].

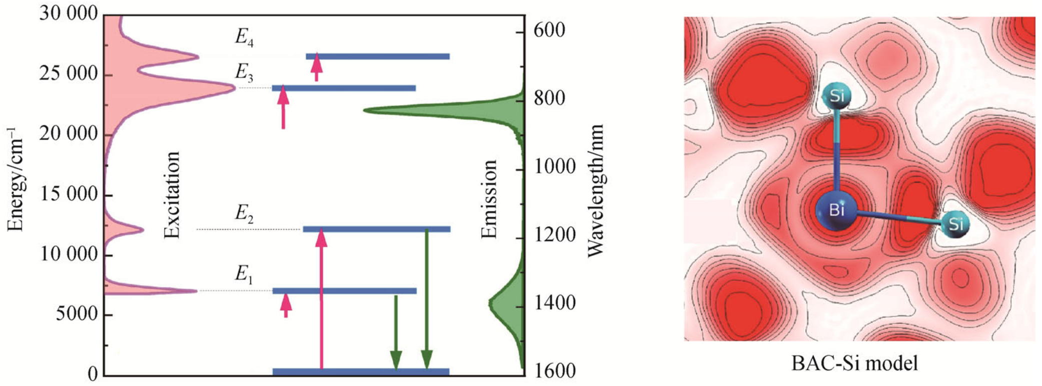
The paper[106] describes the hidden potential of bismuth-doped fibers due to the presence of “dark” precursors, which are certain Bi-related forms that can be transformed into an active state with appropriate treatment. The concentration of such precursors can exceed that of BACs by 5–6 times in an as-fabricated Bi-doped germanosilicate fiber. The authors have experimentally demonstrated that these precursors can be converted into active centers via optimal thermal treatment, significantly increasing the total BAC concentration. Furthermore, it has been shown that this latent potential varies depending on the specific fabrication parameters.

3 Polarization-dependent characteristics of BACs

As mentioned previously, the unique properties of bismuth-doped fibers are attributed to BACs. Their atomic structure has been studied through modeling and in-depth experiments investigating their optical properties and temperature- or photo-induced behavior (*e.g.*,[106–108]). To date, a clearer understanding has been established: a BAC consists of a reduced Bi ion adjacent to a point defect in the glass network, such as an oxygen vacancy (≡Si—Si≡ or ≡Ge—Ge≡). This structural model has been confirmed in the work of various researchers. A typical computational representation of the BAC-Si structure is shown in Fig. 7a and Fig. 7b, along with a diagram of its energy levels.

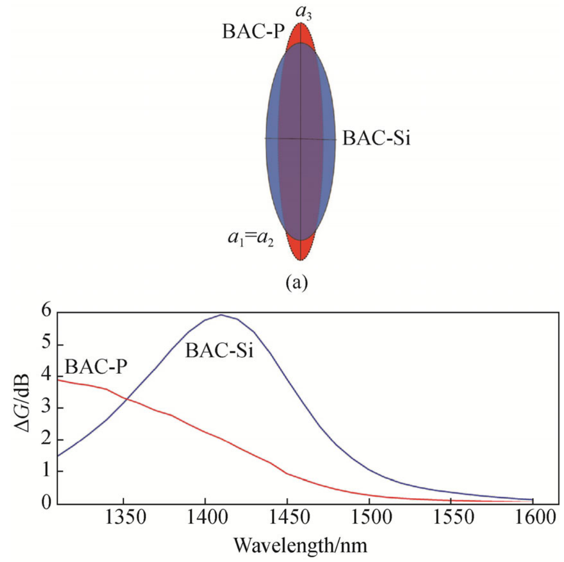
It should be noted that experimental data and additional calculations have shown that a similar structure of the BAC is also characteristic of other types of active centers, such as BAC-P, BAC-Ge[6], and BAC-Al[107].

Recently, the polarization properties of BAC-Si and BAC-P in glass preform samples have been studied in detail. This research has revealed the structural features of these centers[109]. The anisotropic oscillator model was used to analyze the polarization properties of these luminescent centers. This model characterizes the degree of luminescence polarization relative to the orientation of partially anisotropic absorption and emission oscillators responsible for the respective transitions. To describe the properties of the BACs, a partially anisotropic oscillator was used, which is represented by an ellipsoid principal axes, a_1, a_2, and a_3 (a schematic view is shown in Fig. 8a).



(a) (b)

Fig. 7 (a) Empirically obtained levels and transitions schemes of centers; (b) Calculated electron density maps of the centers formed by Bi interstitial atom and oxygen vacancy: Bi^0 and ≡Si−Si≡ vacancy in SiO_2 [107]



(a)

(b)

Fig. 8 (a) Ellipsoids representing partially anisotropic oscillators of BAC-P and BAC-Si for the luminescence under resonant excitation; (b) Gain difference (for orthogonally perpendicular signal polarization states) spectra of amplifiers based on optical transitions of BAC-P and BAC-Si[110]

Consequently, it was found that the degree of luminescence polarization for BAC-P and BAC-Si was 19% and 9%, respectively. The ratio of the minor to major axes of the ellipsoid (under the condition a_1=a_2) was 5 and 3, respectively. This anisotropic nature of the BACs can significantly affect the optical gain for a polarized signal, as shown in Fig. 8b[110].

Thus, the anisotropy of the BACs can have a significant impact on the stability and performance of fiber-optic amplifiers. In the next section, we will briefly discuss the types and main performance parameters of Bi-doped fiber amplifiers.

4 Bismuth-doped fiber-based amplifiers for advanced optical technologies

Bismuth-doped optical fibers are currently being actively used to create fiber-optic amplifiers for a variety of practical applications. These devices are crucial for developing high-speed multiband optical communication systems capable of transitioning from Gb/s to Tb/s data rates, requiring optical amplification across all telecommunication bands from the T- to U-band. Such technologies are essential for high-speed data exchange between data centers, which are being developed to support artificial intelligence systems. Telecom companies are also expected to deploy these amplifiers in future mobile fronthaul networks[111]. The adoption of multiband transmission by a consortium of research institutes and telecommunications companies has enabled the achievement of record values in data transfer rates exceeding 400 Tbit/s over standard fiber. Consequently, there has been significant recent work on developing Bi-doped fiber amplifiers for the O-band. In this band, traditional fiber-optic communication networks exhibit zero dispersion, eliminating the need for dispersion per compensators, significantly reducing the cost transmitted bit. This has led to the development of a series of commercial amplifiers by various manufacturers, such as Amonics, Viavi Solutions, FiberLabs Inc., MPB Communications, Innolume and others. It is also important to note the intensive ongoing efforts to develop bismuth-doped amplifiers operating in other wavelength regions (E-, S-, and U-bands). This progress provides strong grounds for optimism regarding the development of practical ultra-wideband data transmission systems that will incorporate these amplifiers among other technologies. Table 2 summarizes the key parameters of existing Bi-doped amplifiers that have been developed and tested by various institutes and companies.

Table 2　Main parameters of Bi-doped fiber amplifiers

Telecom band	Gain/dB	NF/dB	Bandwidth (at –3 dB level)/nm	Year	Ref.
E	24	6.0	36	2011	[112]
T	12			2015	[113]
U	23	7.0	40	2016	[114]
O	26	5.0	40	2016	[115]
O	31	7.0	30	2019	[116]
O	39	5.0	20	2019	[117]
O	41	4.2	35	2019	[118]
O	40	4.8	35	2019	[119]
O	17	6.0	35	2019	[120]
O	15		100	2020	[121]
O	27	5.0	50	2020	[122]
O	30	7.0	70	2020	[123]
O+E	26	7.3	135	2020	[124]
E+S	28	5.0		2020	[125]
O+E	31	4.8	115	2021	[126]
E+S	31	4.8	30	2021	[127]
O+E	33	5.8	115	2021	[128]
O+E	26	5.0	115	2021	[129]
E	38	6.0	40	2021	[130]
E	30	7.0	40	2022	[131]
O+E	25	8.0	130	2022	[132]
E	38	4.5	75	2022	[133]
O+E+S	29	5.0	120	2023	[134]
O	20	5.5	60	2022	[135]
E	~20	4.6		2022	[136]
O	42	5.8	30	2023	[137]
E+S	20	4.5–6.0		2023	[138]
O+E	41			2023	[139]
O	30	3.7		2023	[140]
E+S	21	5.5	40	2023	[141]
E+S	23	5.5	40	2023	[142]
E+S	43	4.2	25	2023	[143]
O	30	7.0	25	2023	[100]
O	38	6.4	~40	2023	[144]
E+S	49	5.1	20	2025	[105]
O+E	38	3.7		2024	[98]
E+S	48			2024	[145]
O+E	14&16	8.6&10.8	20&40	2024	[146]
O+E	21	9.8	50	2024	[147]
E+S	40	6.0	30	2024	[148]
E+S	39	6.2	25	2024	[99]
E+S	40	5.6	40	2024	[149]
O+E+S	38	4.7	60	2024	[97]
O+E	40&37	5.0	20&25	2024	[150]
O+E+S	34&37			2025	[151]
O	29			2025	[152]
S	42	7.4	20	2025	[153]
E	43	5.5	30	2025	[154]
O	17	7.0	40	2025	[155]

5　Summary

We have reviewed the research progress on bismuth-doped materials, including the current state-of-the-art of Bi-doped fibers for advanced optical devices. New approaches to improving the performance of Bi-doped glasses and fibers were discussed, such as increasing the BACs concentration and reducing the clustering through modulation of topological order, coordination engineering, cluster control and strategies involving “dark precursors” and smart confined doping. Furthermore, recent experimental data on the polarization-dependent properties of Bi-doped fibers were presented, shedding light on the physical nature of the active centers. We also considered novel designs and synthesis methods, such as the “melt-in-melt” technique—in which one molten glass is poured into another at high temperatures—and the controlled, spatially separated formation of different BACs within a heterogeneous Bi-activated core by using varied glass compositions. Additionally, a brief overview of the main parameters of existing Bi-doped fiber amplifiers operating in the O-, E-, S-, and U-bands was provided. Given the progress in this field, future research should focus on further exploratory studies of Bi-doped glass fibers, aiming to enhance the characteristics of existing fibers or to develop new fiber designs for reliable, efficient, and low-cost ultra-broadband optical amplifiers. Based on this review, we can conclude that bismuth is a “wonder” metal that imparts unique and advantageous properties to optical materials, making it highly promising for next-generation fiber photonic technologies. Moreover, it should be noted that bismuth-doped fibers and related optical amplifiers for the O- and E-bands are already commercially available products, used to address scientific and practical challenges, particularly in telecommunications. We believe that the progress made in this area will soon lead to the development of optical communication systems with significantly extended transmission bandwidth, in which Bi-doped amplifiers can be effectively implemented.

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作者贡献声明：

ELOPOV Alexander，RIUMKIN Konstantin，KHEGAI Aleksandr，ALYSHEV Sergey：绘制图表，调查研究，数据管理和分析，初稿撰写，审阅与修订；

FIRSTOV Sergei：论文构思，验证，监督指导，审阅与修订。

Bismuth (Bi): A Wonder Metal Imparting "Magic" Properties to Optical Materials for Fiber Photonic Technologies

ELOPOV Alexander, *RIUMKIN Konstantin*, *KHEGAI Aleksandr*, *ALYSHEV Sergey*, *FIRSTOV Sergei*
(Prokhorov General Physics Institute of the Russian Academy of Sciences, Dianov Fiber Optics Research Center,
Moscow 119333, Russia)

Extended Abstract

Tremendous advances in high-speed communications technologies have enabled modern services, including live 4K video streaming, real-time remote surgery, artificial intelligence (AI), the Internet of Things (IoT), virtual reality (VR), cloud storage, and social media. The further development of these digital platforms will inevitably require increased data transmission rate, which significantly exceed the current capabilities of existing high-speed communications systems. To meet the ever-growing data traffic, it is necessary to develop and implement new advanced solutions. Multi-wavelength transmission technology is considered one of the most promising approaches, which can potentially increase a bandwidth of transmission data over optical fiber systems by utilizing an extended range of wavelengths (from O- to U-band), where the optical loss of conventional single-mode fiber is below 0.2–0.3 dB/km. However, the success of this approach depends on the development of new amplification technologies, as traditional optical amplifiers based on fibers doped with rare earth ions, especially Er^{3+} ions, are inherently incapable of providing effective amplification beyond the C+L telecom bands. This has spurred research into promising amplification media, which began more than 20 years ago.

Bismuth (Bi)-doped fibers (BDFs) are a unique active medium suitable for optical amplifiers and lasers operating in a spectral range of 1.15–1.78 μm. The progress achieved in the development of BDFs and optical devices based on them gives hope that multi-band technologies capable of operating over the entire available spectral range can be successfully implemented in the near future. This is confirmed by the presence of commercially available devices developed by a number of telecom companies, as well as the start of implementation of bismuth-doped fiber amplifiers (BDFAs) for O-, E-, and S-band data transmission over optical communication systems. However, the progress achieved in the development of BDFA and BDF lasers was due not only to the solution of applied problems, but also to a deeper understanding of the fundamental principles of formation of bismuth active centers (BACs) and their physical nature. This review presents the main achievements in terms of optical characteristics of Bi-doped materials (crystals, ceramics, bulk glasses and optical fibers) and devices developed using these materials. This highlights that the structure and chemical composition of the glass matrix strongly influence the resulting optical properties of these media. Some fabrication strategies such as the modulation of topological order, coordination engineering, smart confined doping, and direct cluster control, and novel approaches for performance analysis (for example, “hidden potential”) of BDFs are emphasized and discussed. The peculiar properties of bismuth active centers (BACs), in particular, optical anisotropy and "dark precursors", characterizing their structure and possible process leading to their formation are considered. Also, this review evaluates novel designs of BDFs, especially, heterogeneous glass-core fibers, which can be used for solution of the practical problems. For instance, such designs can be useful for developing a broadband flattop optical amplifier with adopted characteristics. In addition to bismuth-doped materials, this review includes the mainstream results in BDFAs for advanced optical technologies, summarizing the obtained results over two decades. Despite the significant progress the prospects for commercial production of BDFs remain uncertain that primarily due to difficulties in the reproducibility of Bi-doped fiber parameters and the high level of unsaturable loss in highly Bi-concentrated fibers. Addressing these challenges is essential to advancing commercialization and ensuring rapid deployment of this technology.

Summary and Prospects Bismuth-doped fibers (BDFs) have already proven themselves as active materials that can be used to develop optical devices with unique characteristics in previously inaccessible spectral ranges. Optical amplifiers based on these active fibers exhibit high gain and low noise across all telecommunication spectral bands (from O- to U-band), while BDF-based lasers offer the benefits of high efficiency and wide wavelength tunability. However, existing research still faces significant challenges in achieving a reliable technology for reproducing the parameters of BDFs, as well as in fabricating optical fibers with increased Bi concentrations and low unsaturable losses. Developing a high-gain, ultra-wideband amplifier that can be effectively integrated into existing communication systems remains a challenge. Future research should focus on balancing cost, energy efficiency, and device performance, which can be partially addressed by optimizing the BDF design and the device itself. All of this is necessary to meet the growing demand for high-speed data transmission over fiber-optic communication systems, which is crucial in the context of rapidly evolving artificial intelligence technologies. In this regard, the ability to utilize all available telecommunications bands appears very promising. We believe that progress in this area will undoubtedly lead to the development of optical communication systems with significantly increased bandwidth, where bismuth-doped optical amplifiers are key components. Moreover, thanks to ongoing advances in optical materials and process technology, bismuth-doped fiber technology can pave the way for efficient, reliable, and scalable solutions for next-generation fiber-optic systems.

Keywords　optical materials; optical fibers; ceramics; glass; bismuth; luminescence; amplifier; laser device