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Introductory Chapter: Bismuth-Related Optoelectronic Materials

Yanhua Luo, Jianxiang Wen and Jianzhong Zhang

1. Introduction

21st century is the information era. In this rapidly developing information society, more and more optoelectronic materials are needed to meet the increasing demands, including the information generation, transmission, amplification, detection, storage, etc. Among many optoelectronic materials, Bi-related optoelectronic materials are an essential category. The unique properties of bismuth enable the diversity of functions and applications. As schemed in **Figure 1**, bismuth related optoelectronic materials have demonstrated the great potential for the photon generation, amplification, detection and storage. For example, Bi-doped optical fibers (BDFs) have already been proved as the promising active media for the creation of BDF lasers and amplifiers in the near infrared (NIR) region from 1150 to 1800 nm, including the regions of 1250 – 1500 nm and 1600-1800 nm, where efficient rare-earth fiber lasers are absent [1]. In addition, Bi/Er and Bi/Er/Yb co-doped optical fiber (BEDF and BEYDF) have further been developed for broader bandwidth [2, 3]. The BDF lasers can cover O, E, S, C, L and U bands, which are commonly used for fiber-optic telecommunication [4, 5]. The optical amplification in O, E, S, C, L and U bands have also been achieved in both BDFs and BEDFs [6–8]. Regarding to the commercialized bismuth-doped fiber amplifier (BDFA), OFS company reported that the BDFA operating over the O-band (1272-1310 nm) extend 425 Gb/s 400GBASE-LR8 transmission beyond 50 km of G.652 fiber [8]. In the detection field, high performance of the broadband photo detecting have been realized in many bismuth related materials, like bismuth selenide nanowire [9], bismuth telluride nanoplate [10], bismuth sulfide nanobelt [11], bismuth nanosheet [12], and bismuth film [13]. In addition, bismuth halide perovskites have been demonstrated as one of the most efficient and promising solar cells for its free of toxic Pb [14]. Bismuth thin film [15], bismuth tellurite [16], bismuth-substituted iron garnet [17], etc. have exhibited great potential for data storage. In addition, both Bi³⁺ substituted spinel nanoparticles [18] and multiferroic BiFeO₃ [19] can be used for the data storage.

The applications of bismuth related optoelectronic materials above are mainly derived from the unique characteristics of bismuth. It is well known that bismuth is a post-transition metal element. Bismuth and its ions have multivalent states ranged from +5 to 0, or even negative valence [20]. Its ions belong to 6p ions, whose valence state is easily changed, particularly under high temperature and reduction atmosphere [21]. Generally, Bi oxides are likely amphoteric (acidic - basic) for lower valence or acidic for higher valence [22]. As Bi⁸² and Pb⁸³ are located nearby with each other on the periodic table, they have many isoelectronic configurations, e.g. Pb and Bi⁺, Pb⁺ and Bi²⁺, and Pb²⁺ and Bi³⁺. Isoelectronic configurations not



Figure 1.
The functionality of bismuth related optoelectronic materials.

only allow the replacement of Pb with Bi, but also make their properties similar, including density of their doped borate glasses [23], capability to generate the non-bridging oxygens [24], diamagnetic property [25], the analogy of the photoluminescence [21], etc.

Although there are many reports of bismuth related optoelectronic materials at present, this book mainly focuses on their applications for the photon generation, amplification, detection and storage. The whole book can be structured into three sections:

Section 1: Since the first demonstration of broad NIR luminescence in Bi doped silica glass in 1999 [26], BDF and BEDF has been developed for the full utilization of the huge unused bandwidth of the existing telecommunication network, in response to the forecasted upcoming ‘capacity crunch’. In this section, the development of BDF and the post-treatment effect by radiations, like laser, gamma ray and electron beam have been described. Firstly, R. M. D. Alsingery et al. gave an overview of the development of BDFs and their applications in the optical communication system. Then, B. Zhang et al. systematically summarized the photobleaching effect of bismuth active centers (BACs) related to the NIR luminescence in BDF and BEDF, in terms of irradiation intensity/wavelength and temperature. Subsequently, J. Wen et al. fabricated Bi co-doped silica optical fibers with atomic layer deposition (ALD) and modified chemical vapor deposition (MCVD). In addition, gamma radiation effect upon the fluorescence intensity/lifetime, the absorption, as well as Verdet constants of BDFs fabricated have been investigated. Finally, A. Kir’yanov et al. studied effects of electron irradiation on optical properties of bismuth doped phosphosilicate fiber. The results reveal its overall resistance to irradiation in terms of emission and bleaching contrast at excitation into the absorption bands of BACs. In addition, they found a new effect of large dose-dependent Stokes shift, experienced by the fiber’s cutoff wavelength due to the radiation induced refractive-index rise in its core area. The studies of these researchers not only give more information about the configuration and structure of BACs, but also offer an effective approach to regulate BACs.

Section 2: In response to the energy crisis, more and more photovoltaic materials are developed. In recent years, the perovskite solar cells were developed with an excellent power conversion efficiency of 25%, which has been considered as one of the most efficient and promising solar cells. To overcome the remaining issues, like

the presence of highly toxic lead and poor stability, bismuth has been introduced to replace Pb in perovskite solar cells due to their similar property. In this section, K. Ahmad overviewed the fabrication of bismuth halide perovskite solar cells. At the end, some strategies for the improved performance are prospected.

Section 3: In recent years, with the rapid development of optical fiber communication networks, Internet of Things, big data and cloud computing, the amount of global data has shown the exponential growth. The global data volume has already exceeded 45 ZB in 2019, and it is expected to reach 175 ZB in 2025 [27]. To meet the ever-increasing data storage, it is very important to develop the new generation of data storage media for computing performance and the magnetic random access memories storage. In this section, K. C. Verma and J. Angadi described the synthesis and characterization of two bismuth related data storage materials: multiferroic BiFeO₃ and Bi³⁺ doped manganese spinel ferrite nanoparticles, respectively.

The ferroelectricity of BiFeO₃ is originated from 6s² lone-pair electrons of Bi³⁺ and the G-type antiferromagnetic ordering resulted from Fe³⁺ spins order of cycloidal below Neel temperature. So multiferroic BiFeO₃ allows the data to be written electrically and read magnetically due to its magnetoelectric effect observed at room temperature. Especially, the structure of BiFeO₃ can be controlled through the selection of appropriate synthesis route, reaction conditions and heating processes. To overcome the drawback of the disappearance of multiferroicity in BiFeO₃, several solutions are proposed like the replacement of dopant ions, the control of ions concentration, BiFeO₃ composites as well as thin films, especially multilayer structures.

The Mn_{1-x}Bi_xFe₂O₄ (x = 0.0, 0.05, 0.1, 0.15 and 0.2) nanoparticles were prepared by the solution combustion method and their structural, microstructural and magnetic properties are characterized. Rietveld refined X-ray diffraction (XRD) patterns confirm the single-phase formation with space group Fd3m having spinel cubic structure and the lattice parameters increase with the increase of Bi³⁺ concentration. The magnetic hysteresis curves reveal the soft magnetic material nature of these nanoparticles, demonstrating the great potential for absorbing electromagnetic waves, storage media, etc.

As the most promising gain medium for the next generation photonic network, the work presented in the Section 1 is evidently not enough. So, challenges and opportunities of the development of BDF and BEDF is further briefed in the following.

2. Challenges and opportunities of bismuth doped optical fiber

2.1 Background

Water-free fiber technology has enabled silica optical fibers to achieve ultra-low loss transmission over the broad spectral range of 1200-1700 nm, where the transmission loss is less than 0.5 dB/km as shown in **Figure 2** [28]. **Figure 2** also shows the NIR spectral range of some rare earth ions often doped in fibers [28]. It has already demonstrated that the construction of the efficient optical amplifiers based on rare earths doped optical fibers for the extended bands is impossible. Though many researchers have previously been focused on the development of fiber amplifiers and lasers based on fibers doped with rare earth ions, e. g. Er³⁺, Tm³⁺, Yb³⁺, Nd³⁺, Ho³⁺, Pr³⁺, for the extended bands, none of them has demonstrated sufficient optical gain and enough bandwidth for the telecommunication applications.

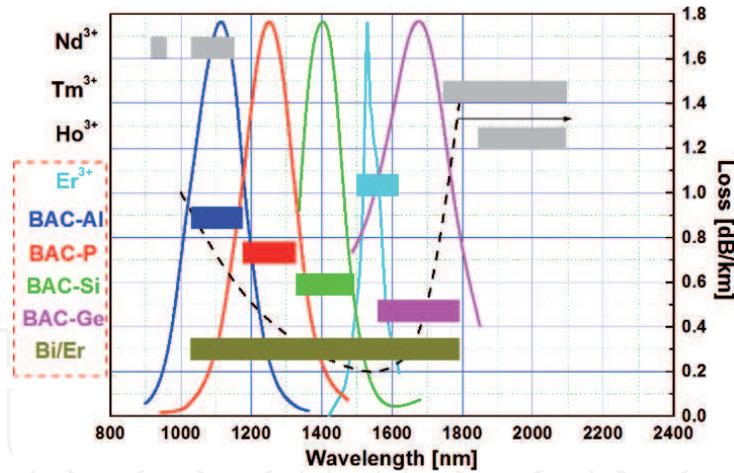


Figure 2.

Spectral ranges of various doping elements, normalized emission spectra from each active center interested as well as the low-loss spectrum of silica-based optical fiber.

Since the first demonstration of broadband NIR luminescence in Bi-doped silica glass [26], many researchers have devoted to the investigation of bismuth doped glasses or materials for the extended band [29–31]. The development in these materials has spurred significant work in optical fiber form [28, 32], since the fabrication of the first BDF in 2005 [33]. Different from the well shielded shell of rare earth ions, the electronic shell of bismuth is easy coupled with the external environment, which finally influences the characteristic properties of BACs. According to the local environments, there exist four types of BACs, which are BAC-Si, BAC-Ge, BAC-P and BAC-Al, relating to SiO_2 , GeO_2 , $\text{P}_2\text{O}_5:\text{SiO}_2$ and $\text{Al}_2\text{O}_3:\text{SiO}_2$, respectively [5]. The normalized luminescence spectra of these four BACs are plotted in **Figure 2** [34]. Seen from **Figure 2**, BDFs have demonstrated as the promising active media for the NIR region from 1150 to 1800 nm [1]. Especially, through their co-doping, more broader and stronger emission and gain can be achieved, like Bi/Er [7, 35–37], Bi/Tm [38, 39], etc. [40, 41].

2.2 Remaining challenges

Despite the great success in the development of the BDF technology for the unused bandwidth, there remain many fundamental scientific and technological issues and challenges, before these fiber lasers and amplifiers can be practically and commercially used.

On the scientific side: The main challenge is that the nature of bismuth NIR emitting centers is still not clear [1]. Difficulties mainly arise from Bi where its d orbitals are easily coupled to the surrounding environment. But it is such coupling, which allows the formation of broadband NIR emission center through the tailoring of the external environment by additional dopants such as Ge, P, Al, etc. Meanwhile, bismuth as the wonder metal, can proceed reduction reactions with no other element and produce such a variety of products [42]. Especially, under the high temperature, the change of the valent state of bismuth in Bi-doped glasses occurs [43]: $\text{Bi}^{3+} \rightarrow \text{Bi}^{2+} \rightarrow \text{Bi}^+ \rightarrow \text{Bi}/\text{Bi}_2, \text{Bi}_2^-, \text{Bi}_3, \text{etc.} \rightarrow (\text{Bi})_n$, where $\text{Bi}_2, \text{Bi}_2^-, \text{Bi}_3, \text{etc.}$ are Bi clusters and $(\text{Bi})_n$ is metallic colloid. As bismuth doped glasses and fibers often undergo the high temperature in the fabrication process. For example, under the high temperature treatment, the color of the doped core in the BEDF preform is clearly changed as indicated in **Figure 3** (the dark color is often taken as the evidence of the formation of $(\text{Bi})_n$). So many types of bismuth often co-exist in these Bi doped glasses and fibers. Their properties, like unpaired electrons, radius and fluorescence lifetime are different with each other as listed in **Table 1**.

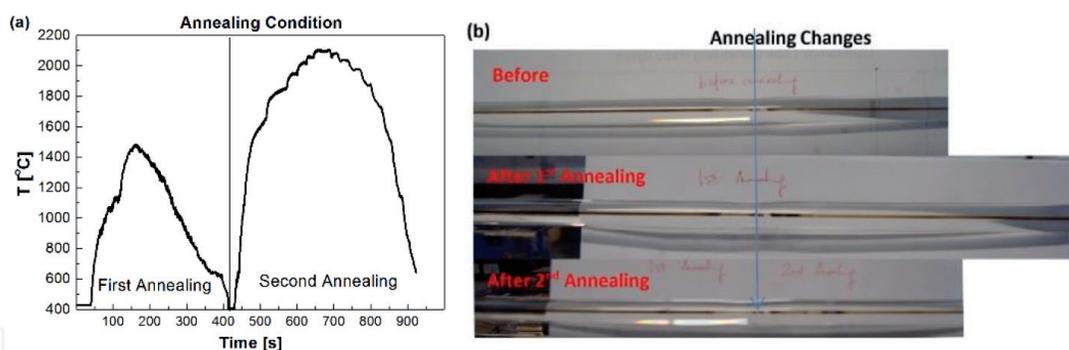


Figure 3. Thermal treatment influence upon the fiber core in the BEDF preform: (a) annealing conditions; (b) the color change in the core part with thermal treatment.

Valence	Configuration	Number of unpair electrons [44]	Radius [Å] [45]	Lifetime [μs] [46]	
				NIR	Visi
Bi ⁰⁺	[Xe]5d ¹⁰ 6s ² 6p ³	3	1.56	≥10 ²	~10
Bi ¹⁺	[Xe]5d ¹⁰ 6s ² 6p ²	2	1.45	~10 ²	≥10
Bi ²⁺	[Xe]5d ¹⁰ 6s ² 6p ¹	1	1.16	—	~10
Bi ³⁺	[Xe]5d ¹⁰ 6s ²	0	0.96	—	1
Bi ⁴⁺	[Xe]5d ¹⁰ 6s ¹	1	—	—	—
Bi ⁵⁺	[Xe]5d ¹⁰	0	0.74	—	—
Bi ⁶⁺	[Xe]5d ⁹	1	—	—	—
BiO	—	—	1.70	≥10 ²	≥10
Bi ₂ ⁻	—	—	—	≥10 ²	~10

Table 1. Unpaired electrons, radius and fluorescence lifetime of bismuth ions.

So far, a number of hypotheses are reported about the origin of the NIR emission center in Bi-doped glasses, like: Bi⁺, Bi⁵⁺, Bi⁻ clusters, BiO, Bi₂⁻, Bi₂²⁻ point defects and others, but none of them have been directly confirmed [1]. Though the recent report by Dianov et al. has confirmed that Bi-related NIR emitting centers are clusters consisting of Bi ions and oxygen deficiency centers instead of Bi ions themselves [1], the exact form of bismuth in BAC remains unclear. In addition, the NIR luminescence has also been observed from Bi-doped CsI halide crystals [47], fluoride glasses [48], etc. where no oxygen deficiency will exist in these materials. Therefore, to conquer this challenge, further research is necessary to get reliable results on the nature of Bi-related NIR emitting centers in Bi-doped glasses and optical fibers of various compositions and fabrication techniques with different processing conditions.

On the technological side: As the valence state of Bi in BDF/BEDF will change during the fabrication process, so it becomes a technical challenge to control the formation rate of BAC for the preparation of optical fibers. Both the valence state of bismuth and oxygen deficiency centers are sensitive to the processing temperature [43, 49]. In addition, bismuth oxide is easier evaporated during the collapsing process of preform fabrication with the MCVD technique compared with rare earth oxide. Hence, the control of the valence state of Bi as well as the formation rate of BAC is hardly achieved in BDF/BEDF. So there often co-exist many types of Bi ions or BAC in Bi-doped materials [50]. Though the full control of the formation of

BACs is very hard, reductive agents, like high-purity silicon powder or sucrose in MCVD process [51] and SiC in melt and pour glass [52] have already been introduced in the fabrication of the Bi-doped materials as bismuth NIR emitting centers are formed in an endothermic redox chemical reaction [53]. In addition, post treatments, like femtosecond laser [54], thermal treatment [55, 56], γ -radiation [57], H_2 reduction [58], etc. have also been tried to activate and control the BAC. Recently, M. Melkumov et al. have tried to improve the performance of BDF by the optimization of drawing and MCVD processing conditions [59, 60]. Though these solutions can regulate the formation of BAC to some degree, the success rate still cannot be quantified due to the unclear structure of the BAC. In addition, most of BDFs with lasing and amplification are doped with very low content of bismuth (usually <0.1 wt.%) [5], which is often lower than the detection limit of mostly used equipment-energy-dispersive X-ray (EDX) analyzer. However, the performance improvement by the increment of Bi concentration is limited by the fast growth of the background loss in fiber [5]. So the concentration increment and the control growth of the background loss should be balanced for high performance BDF and BEDF. All these technical issues are subject to further in-depth and systematic research and development, such as the selection of dopants and their compositions, and fabrication conditions, etc.

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