Ultra-broadband luminescent sources that emit light over an extremely wide wavelength range are of great interest in the fields of photonics, medical treatment, and precision measurement. Extensive research has been conducted on materials doped with rare-earth and transition-metal ions, but the goal of fabricating an ultra-broadband emitter has not been attained. We present a facile method to realize this kind of novel light source by stabilizing “active” centers (bismuth) in a “tolerant” host (nanoporous silica glass). The obtained highly transparent materials, in which, unusually, multiple bismuth centers (Bi\(^{+}\), Bi\(^{2+}\), and Bi\(^{3+}\)) can be stabilized, emit in an ultra-broadband wavelength range from blue-green, orange, red, and white to the near-infrared region. This tunable luminescence covers the spectral range of the traditional three primary colors (RGB) and also the telecommunications windows.

1. Introduction

Luminescent materials doped with isolated active centers find great applicability in displays, lighting, lasers, optical telecommunications, and various other fields.\(^{[1–5]}\) Because of the rapid development of technology, needs in these fields are not well met and they present new challenges for traditional phosphors. A typical case is that the mature single blue-, green-, and red-light-emitting components raise difficulties in device integration.\(^{[6]}\) In addition, the limited range of infrared light sources also hinders the development of optical communications technology.\(^{[3,7]}\) The increase in optical communications traffic has stimulated a breakthrough in dry fiber fabrication; this progress has opened the possibility for using fiber bandwidths all the way from 1.3 to 1.6\( \mu m \). Unfortunately, at present there are no efficient broadband optical amplifiers that can cover the bandwidth from 1.3 to 1.6\( \mu m \). The development of novel tunable broadband light sources holds considerable promise for solving these problems.\(^{[8]}\) Lanthanide-activated luminescent materials have been explored as multifunctional light sources, but the emission originating from 4f–4f transitions shows sharp emission peaks at specific bands, and multilayer devices lead to high manufacturing costs.\(^{[9]}\) Transition-metal ions activated hybrid materials give rise to broader luminescence, but their emission covers only discontinuous bands.\(^{[10–12]}\) Hence it remains a challenge to fabricate an ultra-broadband light source with multifunction.

Our approach to creating a tunable broadband light source involves two design parameters: the “active” dopant with multiple emission centers and the “tolerant” hosts to stabilize them. The activity of the dopant can be considered from the viewpoint of electron configuration. For lanthanide ions (4f configuration) and transition-metal ions (3d configuration) in a solid, the spin–orbit interaction and the crystal field take the dominant role in the energy level distribution. Somewhat differently, the level analysis of main-group ions with\(^{[13]}\) nsnp configuration must take into account the multiple factors of spin–orbit interaction, the crystal field, and the additional electrostatic interaction. This can be explained by the extended nature of their np orbitals. Furthermore, the valence states of these ions change between M\(^{n+}\) (ns\(^2\)np\(^n\)) and M\(^{n+}\) (ns\(^{n+}\)np\(^{n+}\)).
(ns^n) (where M and ns^nnp^3 represent the kind of ion and the outerlayer electronic configuration, respectively), depending on their chemical environments. These characteristics imply that many parameters can be tuned to control their optical properties, and it would be expected that potential multiple and even novel emission centers can be acquired with these ions. The other important point is the “tolerant” hosts, which are employed to stabilize these centers. Previously extensive research conducted on crystalline and amorphous materials indicated that substitution of activated ions into specific lattice positions in these hosts is unfavorable to stabilize multiple centers. Therefore, a host capable of providing much greater degrees of freedom for the regulation of the chemical equilibrium of an emission center is necessary.

Applying our design criteria, we report a facile approach to the design and fabrication of a multifunctional broadband light source that exploits a nanocage to stabilize novel bismuth emission centers. This approach to generating multiple centers is realized by conveniently regulating and stabilizing these centers in a nanocage structure, and it overcomes the limitation of the harsh requirement of a particular crystallographic environment for particular ions in crystalline hosts.

Furthermore, the unique properties of nanoporous materials, such as high surface area and special pore structure of varying morphologies, can avoid the clustering of luminescence ions and the concentration quenching effect. We have demonstrated this method with the realization of an ultrabroadband light source covering almost the whole 400–1600 nm region. Because standard thermodynamic and kinetic data can be used to rationally choose preparation conditions, we believe that our approach could be adopted for preparing numerous novel multifunctional luminescent materials.

2. Results and Discussion

Bismuth-doped nanoporous glass was prepared by soaking the nanoporous glass in Bi-containing solutions and then treating it in a special atmosphere. The detailed process can be referred to in the Experimental section and Figure 1. Figure 2 presents the transmission spectra of blank porous glass, Bi-doped samples treated in air (denoted sample A) and argon atmosphere (denoted sample B), respectively. The inset also gives the enlarged spectra and photographs of samples A and B. All these samples are highly transparent. Blank porous glass has high transparency from 250 nm to the infrared region, and therefore it is an excellent matrix for phosphors. In contrast to the blank sample, samples A and B show strong absorption at about 250 nm. In addition, several absorption bands around 350, 430, and 800 nm are also observed in sample B. These peaks are related to multiple Bi centers; the detailed assignments will be discussed below.

Figures 3a and b show the photoluminescence excitation (PLE) and photoluminescence (PL) spectra of samples A and B. (Blank porous glass and Bi-doped porous glass treated in hydrogen atmosphere do not show any emissions.) When excited with a single wavelength at 280 nm, sample A shows intense blue-green luminescence at 465 nm (Fig. 3d), which could be ascribed to the emission band of the Bi^{3+} ion according to the results of Blasse and Bril. In contrast, sample B can be excited with multiple wavelengths of 280, 350, and 483 nm, and from these excitation wavelengths, tunable white, purplish red, and orange luminescence can be realized from the studied material. When excited with 483 nm, sample B emits a single symmetric broad band centered at 590 nm. This kind of unique orange emission character (Fig. 3d) is similar to the emission property of the unusual emission center Bi^{2+}, which has been reported in only a few matrices, for example, SrB_4O_7 (see Fig. 3c). An additional band is observed around 465 nm with 350 nm excitation and this band becomes more obvious when the excitation wavelength is 280 nm. It might be attributed to the Bi^{2+} center as observed in sample A.

Interestingly, two emission bands, centered at 465 nm and 590 nm, are observed in sample B when excited with 280 nm.

Figure 1. Schematic summary of the route to the activated nanoporous glass in this work.

Figure 2. Transmission spectra of blank porous glass, sample A, and sample B. Inset: Enlarged spectra and photographs of samples A (left) and B (right).
The combination of these two bands covers the whole visible spectrum and induces a broadband white-light emission (Fig. 3d). The white-light emission might be activated by co-excitation since both these emission bands have the same origin (280 nm excitation). We also performed luminescence decay measurements for samples A and B, and the results are shown in Figure 3e. For sample A, the monitoring wavelength is 465 nm and the excitation wavelength is 280 nm. The decay curve was fitted by an exponential function and the estimated lifetime is 7.2 μs. For sample B, the monitoring wavelengths are 465 and 590 nm and the corresponding excitation wavelengths are 350 and 483 nm, respectively. Both decay curves were also fitted by exponential functions and the estimated lifetimes are about 6.8 μs (at 465 nm) and 6.3 μs (at 590 nm). These values are similar to the lifetime of the Bi$^{3+}$ and Bi$^{2+}$ centers in crystal hosts.[19,20] The Commission Internationale de l’Eclairage (CIE) chromaticity coordinates for Bi-doped nanoporous glass are presented in Figure 4. It is observed that the (X,Y) coordinates can be controlled systematically from (0.208, 0.318), (0.311, 0.351), and (0.440, 0.280) to (0.575, 0.420), corresponding to tunable blue-green, white, purplish red, and orange luminescence. This kind of tunable visible luminescence has potential multiple functions with applications as a light source for compact display and light systems. Especially the broadband blue-green emission has potential applications in the field of dense optical storage and submarine communications.

It is necessary to point out that the excitation band at 350 nm, which results in the luminescence at 590 nm in sample B, is absent in the PLE spectra of the Bi$^{3+}$ ion in sample A (Fig. 3a) and the Bi$^{2+}$ ion in the SrB$_4$O$_7$ crystal (Fig. 3c). Since there is an additional absorption band around 800 nm in sample B, we have employed an 800 nm laser diode (LD) as excitation source for this sample and detected infrared luminescence. It is interesting that a broadband near-infrared emission can be observed in sample B. As the infrared-active Bi centers also show emission when excited at special bands where no obvious absorption bands are observed,[21] we used other types of LD as excitation sources, and the measured infrared luminescence spectra are presented in Figure 5a. It is

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observed that the wavelength of emission can be controlled easily by changing the excitation wavelength. Infrared luminescence was centered at 1100 nm when excited with 532 and 980 nm, while it was at 1400 nm with 800 nm excitation. By contrast, sample A does not show any infrared emission. The decay curves of the 1100 and 1400 nm emission at room temperature are presented in Figure 5b. Both curves show first-order exponential decay and the lifetimes are 108 and 254 μs, respectively. This broadband emission is very important in the field of fiber optics. As is known, the increase in optical communications traffic is stimulating much research into the development of multiple-wavelength emitters and amplifiers for coarse wavelength-division multiplexing and code-division multiple access. Silica-based transmission fiber has a wide window from 1200 to 1600 nm, and thus there is an emerging demand for optical amplifiers usable in this range. Although extensive research has focused on rare-earth ions (Pr³⁺, Tm³⁺, and Er³⁺) and transition-metal ions (Cr⁴⁺ and Ni²⁺) for the purpose of exploring broadband light sources, the bandwidth is still limited (less than 100 nm for rare-earth ions and about 200 nm for transition-metal ions). The infrared luminescence of sample B peaks beyond 1.3 and 1.5 μm. It is interesting that two emission bands located at different wavelengths can be realized by choosing different excitation sources. The full width at half maximum (FWHM) of the emissions at 1100 and 1400 nm are 205 and 182 nm, respectively. The combination of these two emission bands might potentially bridge commercial amplifiers and can be used as a broadband amplifier.

The characteristic infrared emission with long fluorescent lifetime in sample B is different from the optical properties of Bi²⁺ and Bi³⁺ centers. Therefore, it should be ascribed to another type of active center. Many attempts have been made to prepare infrared-active Bi-doped materials. It was found that co-doping species such as Al and Ta are necessary for stabilizing such infrared-active centers hosted in glasses acquired by the high-temperature melt-quenching method. However, the origin of the infrared luminescence is still unclear and controversial. There has been conflicting evidence as to whether the higher valence Bi or the lower valence Bi contributes to the infrared emission. In this work, we have found that both high and low valence states of Bi are stabilized in the nanopore glass, while the infrared emission was observed only in sample B. This result demonstrates that the infrared emission may be attributed to the electronic transition of low valence state Bi, most probably Bi⁺, rather than a higher valence state.

The schematic energy level diagrams for various Bi valence states are depicted in Figure 6. Bi²⁺ ion has 6s² configuration, and thus the ground state is ⁵S₀ and the excited states are ⁵P₀, ⁵P₁, ⁵P₂, and ⁵P₃ in order of increasing energy. According to dipole selection rules, excitations usually occur from the ⁵S₀ ground state to the ⁵P₁ and ⁵P₃ states. Therefore, the excitation band in the Bi-doped sample A corresponds to the ⁵S₀→⁵P₁ transition, and its blue emission can be ascribed to the ⁵P₁→⁵S₀ transition. Identification of the unusual Bi²⁺ center has been proposed previously. The Bi²⁺ ion has 6s⁶p⁴ configuration, and thus one has to consider a single p electron. The ground state configuration 6s⁶p⁴ is split by spin–orbit coupling interaction into a ⁴S₁/₂ ground state and a ⁴S₃/₂ excited state. The excited state ⁵P₃/₂ is further split by crystal-field interaction into two crystal-field terms, which are denoted as ⁵P₃/₂(1) and ⁵P₃/₂(2) in order of increasing energy. The excitation bands at about 280 and 483 nm in sample B can be ascribed to the ⁵P₃/₂(1) and ⁵P₃/₂(2) transitions, respectively, and the observed orange-red emission can be attributed to the ⁵P₃/₂(1)→⁵P₁/₂ transition. Owing to the disordered structural characteristics, the excitation bands of active centers in glass...
hosts may be broader than that in the crystalline matrix, as shown in Figure 3. The peak position also showed a slight difference, which is mainly caused by the variation of crystal-field strength between the different hosts. In the case of the Bi$^+$ ion, energy level analysis is complicated by the presence of two 6p electrons in the ground-state configuration. The analysis is based on the calculated model for the 6s$^2$6p$^2$ configuration. The mutual electrostatic interaction of two 6p electrons splits the ground term into fine-structure levels: $^3P_0$, $^1P_1$, and $^3P_2$, in ascending order. Three main absorption bands centered at 350, 430 and 800 nm in Figure 2 correspond to the $^3P_0 \rightarrow ^1S_0$, $^3P_0 \rightarrow ^1D_2$, and $^3P_0 \rightarrow ^3P_2$ transitions, respectively. A band in the infrared region resulting from the $^3P_1 \rightarrow ^3P_0$ transition is not obvious in our Bi-doped porous silica glasses, or in other Bi-doped silicate glasses.[29] The $^3P_1$ state has been identified as a metastable emitting state.[13] Unlike the allowed transitions $^1P_1 \rightarrow ^1S_0$ in Bi$^{3+}$ and $^2P_{3/2}(1) \rightarrow ^2P_{1/2}$ in Bi$^{2+}$, the transition $^3P_1 \rightarrow ^3P_0$ in Bi$^+$ is rigorously forbidden and the energy gap is small. As a result, the corresponding radiative transition is located in the near infrared region with long decay lifetime. Accordingly, the Bi$^+$ center shows infrared luminescence with longer decay time. In addition, owing to the extended nature of its 6p orbitals, the crystal field also plays an important role in the luminescent properties. Thus, the excitation-wavelength-dependent infrared luminescence in Figure 5a may be attributed to site-to-site variations in the environment of the emission centers.

In a hybrid system with coexisting multiple centers, energy transfer and co-excitation may also affect the luminescence properties. As shown in Figure 6, the $^1P_1$ level of Bi$^{3+}$ and the $^2S_{1/2}$ level of the Bi$^{2+}$ center are located in the same region between 250 and 280 nm. As a result, co-excitation may be expected to occur when this band is excited, which can be used to explain the white-light emission observed in Figure 3. Furthermore, blue and red emission can also be detected in sample B with 350 nm excitation. However, this is not the case in sample A and SrBa$_4$O$_7$:Bi$^{2+}$. This phenomenon may be due to the energy transfer process from Bi$^+$ ion to Bi$^{3+}$ and Bi$^{2+}$ ions, based on the fact that the $^3P_1$ (Bi$^{3+}$) and $^3P_{3/2}$ (Bi$^{2+}$) levels are lower than the $^1S_0$ level of Bi$^+$.

The unusual valence state luminescent ions have been paid particular attention in crystal matrices.[30–32] It was found that the existence of these are restricted by many parameters, including the type of anions in the compound, the site size, and the energy bandgap.[16] However, there is no report about the kind of ultra-broadband and tunable emission found here in Bi-doped nanoporous silica glass in general dense hosts such as crystalline or even glassy materials. This result suggests that the nanocage-containing porous glass could be considered as an excellent “tolerant” host for fabricating multifunctional and tunable light sources.

In addition, the small, nanometer pores also provide a high degree of freedom for materials design. An outstanding example is the Bi$^+$ center, which has, to the best of our knowledge, never been reported in crystal matrices. Taking into account the position of Bi in the periodic table, this might be due to the large ionic radius of Bi$^+$ (comparable to Rb and Cs ions), and that it is inherently difficult to stabilize in common coordination geometry.

Figure 7. a) TEM image of Bi-doped porous glass treated in hydrogen atmosphere (the full scale of the image is 628 nm). The arrows indicate the nanoparticles. b) Spatially resolved EELS on particle and on glass as indicated in (a). The peak at 15 eV is the Bi bulk plasmon. The major peak at about 24–25 eV is the bulk plasmon of SiO$_2$. c) TEM image of a single nanoparticle (the full scale of the image is 153 nm). Inset: Corresponding diffraction pattern.
Besides the controllable super-broadband visible-infrared emission, nanoporous matrices can also potentially be used as templates for in situ preparation of nanoentities.[33,34] We also acquired phase-pure bismuth nanoparticles in the sample treated in hydrogen atmosphere. Figures 7a and c show transmission electron microscopy (TEM) images of nanoparticles in the porous glass, and the inset of Figure 7c gives the diffraction pattern of a nanoparticle, which can be indexed as a Bi crystal. Spatially resolved electron energy loss spectroscopy (EELS), on and off a particle was also carried out and the results are presented in Figure 7b. The peak at 15 eV corresponds to the Bi crystal plasmon, and the major peak at about 24–25 eV is the bulk plasmon of SiO2. The results are consistent with the previous TEM data. Bismuth is a semimetal, and its relatively low melting point (574 K) makes it attractive for thermally induced phase transformations.[35]

This characteristic has important applications for thermal-optical switching,[36] light-induced reflectivity tuning,[37] and enhancement of second-harmonic generation.[38] However, despite its attractive properties, its performance is still limited due to the scarcity of hosts with high thermal resistance. The prepared nanoporous glass with composition of nearly pure SiO2 may show high toughness for thermal loading and the hybrid material has potential applications in the above-mentioned fields. The next research step will focus on these properties.

3. Conclusions

In summary, we have demonstrated that multivalent bismuth nanocrystals can be stabilized effectively within the nanoporous structure in porous silica glass. The novel hybrid system shows multicolor luminescence from blue-green, orange, red, and white to the near-infrared region and it can be potentially applied as a wide-spectrum light source. The luminescence mechanism is also discussed and the results provide evidence that infrared luminescence originates from the low-valence-state Bi. We have also found that nanoporous matrices can potentially be used as templates for in situ preparation of Bi nanocrystals. This might be attractive because of its multiple physical effects, such as thermal-optical switching, light-induced reflectivity tuning, and enhancement of second-harmonic generation. It is believed that the Bi-doped nanoporous glass thus obtained shows optical performance superior to that in other matrices. We propose that immobilizing active centers in a nanocage structure provides a new platform for design and fabrication of novel transparent photonic materials.

4. Experimental

The preparation process involves two steps: regulation of the chemical equilibrium of various Bi centers in a nanocage structure by controlling the parameters (temperature, atmosphere), and then retaining the special nonequilibrium state at room temperature by collapsing the cage. The nanoporous silica glass is adopted as the matrix since it can be consolidated easily and it also has some other desired properties such as transparency, easy fabrication, high mechanical strength and chemical durability. An alkali borosilicate glass with the composition 61.5SiO2-27B2O3-8.5Na2O-3Al2O3 (in wt%) was used to prepare a nanoporous host by a melt-quenching technique. Batches of ca. 50 g were mixed homogeneously in an agate mortar and melted in a Pt-Rh crucible in air at 1450 °C for 3–4 h. The melt was then cast into a slab on a heated iron plate. The obtained glass was heat-treated in air at 580 °C for 40 h to cause phase separation. Subsequently, the glass was cut into chips, polished and leached in hot (90 °C) 1 m HNO3 for 48 h. After washing with distilled water and drying, leached porous glass was obtained. Chemical analysis showed that the proportion of SiO2 in the porous glass was greater than 96%. The size of the pores could be tuned conveniently by controlling the preparation process, and the host used in this experiment had nanopores with uniform size of about 20 nm, which was confirmed by TEM. The “thirsty” dry porous glasses were soaked in solutions of 0.2 m Bi(NO3)3 for 2 days. The impregnated samples were then dried at 150 °C for 2 days and subsequently heat-treated at 1000 °C for 1 h at argon, or hydrogen atmosphere. The detailed preparation process is schematically illustrated in Figure 1.

Absorption spectra were recorded by a double-beam spectrophotometer (JASCO FP-6500). The visible luminescence and luminescence decay measurements were obtained by exciting the samples with a 450 W Xe lamp with a double 0.22 m SPEX monochromator. The fluorescence was detected through a 0.5 m monochromator monitored by a Tektronix TDS3052 (scanning) transmission electron microscope operating in TEM mode.

References