

Significantly enhanced superbroadband near infrared emission in bismuth/aluminum doped high-silica zeolite derived nanoparticles

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Abstract: Significantly enhanced superbroadband near infrared emission has been realized in bismuth/aluminum doped high-silica zeolite derived nanoparticles. The emission intensity can be easily tailored by the introduction of aluminum. The luminescence lifetime can reach up to 695 μ s. The results reveal that the existence of charge imbalance environment caused by $[AlO_{4/2}]^-$ units in host materials is requisite to the formation of infrared-active Bi^+ . The finding presents a feasible route to design high-efficient bismuth activated infrared luminescent nanoparticles. These bismuth doped nanoparticles may find applications as superbroadband near infrared nano optical sources.

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1. Introduction

In recent years, extensive studies on bismuth related superbroadband near-infrared (NIR) photoluminescence (PL) have been carried out in traditional glass materials [1-6]. Concurrently, different authors tentatively assigned the NIR emission to the electronic transition of Bi^{5+} , Bi^+ , Bi^{2+} , or to cluster of Bi atoms dispersed in glass host, and the final conclusion has not been made yet [1-6]. In comparison with the studies of Bi doped glasses, little attention has been paid on the investigation of Bi doped crystals [7]. It is well known that spectroscopy of active ions is much more understandable in crystals than in glasses because there is a definite majority of sites for doping ions in crystal. Therefore, finding a suitable crystal as the host of bismuth infrared-active (BiIRA) centres may pave the way for understanding the PL origin.

Zeolites, as smart crystalline materials mainly consisting of $[\text{SiO}_4]$ and $[\text{AlO}_4]$ structure units, possess pore structures and these enable them to act as hosts for molecules and ions or as templates for nanostructures synthesis [8]. Recently, their potential as host materials for rare-earth ions has been evaluated [9]. However, the efficiency of the emitters is very small in the NIR region due to the fast relaxation of the excitation energy through nonradiative vibrational deactivation. Moreover, the obtained samples were not air-stable, which were usually kept in vacuum to avoid the adsorption of coordinated water [9]. Thus, it is an interesting topic to find a strategy to increase the NIR PL efficiency in active ions doped zeolites.

Very recently, we realized above two purposes by using bismuth doped crystalline nanozeolites [10]. The emission band covered the range of 930~1620 nm, with a maximum peak at 1146.3 nm, a full width at the half maximum (FWHM) of 152 nm and a lifetime of over 300 μs under the excitation of a 488 nm laser line. In this paper, we studied the effect of aluminum doping on the NIR emission of bismuth doped zeolite derived nanoparticles. NIR emission has been enhanced significantly by the introduction of aluminum in these nanoparticles. The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), steady-state and time-resolved PL measurements. Based on these results, the origin and enhancement mechanism of PL were discussed in detail.

2. Experimental

The H form of FAU-type zeolites were purchased from Tosoh Co. Japan (Zeolite Y, grain size: 200 ~ 400 nm). Zeolites was stirred in a 0.01 M aqueous solution of Bi^{3+} prepared from $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ at 80 °C for 72 h to exchange H ions with Bi^{3+} ions. The products were removed by centrifugation, and dried in air. The Bi^{3+} embedded zeolites were further stirred in 0.01M Bi^{3+} and $x\text{M Al}^{3+}$ ($x=0.015, 0.025, 0.035$) mixed solution at 80 °C for 24 h to dope Al^{3+} ions. The products were collected by centrifugation, then washed with deionized water, and dried in air at 120 °C. The Bi^{3+} and $\text{Bi}^{3+}/\text{Al}^{3+}$ doped zeolites were calcined at 1150 °C for 20 min in N_2 atmospheric condition. All samples were exposed to the laboratory atmosphere prior to measurements. The prepared products were first characterized by X-ray diffractometer (Rigaku-TTR/S2, $\lambda=0.154056$ nm). The morphologies of the prepared products were characterized using a FE-SEM (JEOL, JSM-6335F) operating at an accelerating voltage of 15 kV. Bismuth and aluminum concentrations were measured by X-ray fluorescence (XRF) and energy-dispersive X-ray spectroscopy (EDS). The atomic ratios of Bi and Al to (Si+Al+Bi) were summarized in Table 1. Note that the Al content in sample 1 is from zeolites. Luminescence measurements were carried out at room temperature with the excitation of a 488 nm line of an Ar^+ laser. The signal was analyzed by a single grating monochromator and detected by a liquid-nitrogen-cooled InGaAs detector. For all the spectra, the spectral

response of the detection system was corrected by the reference spectrum of a standard tungsten lamp. Time-resolved luminescence measurements were performed by detecting the modulated luminescence signal with a photomultiplier tube (Hamamatsu, R5509-72), and then analyzing the signal with a photon-counting multichannel scaler. The excitation source for the lifetime measurements was the 488 nm light from an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser.

Table 1. Determined Bi and Al Ratios of the Samples

Sample no.	Bi ratio (%)	Al ratio (%)	Doped ions
1	0.70	0.27	Bi ³⁺
2	0.47	0.53	Bi ³⁺ /Al ³⁺
3	0.29	0.68	Bi ³⁺ /Al ³⁺
4	0.24	0.73	Bi ³⁺ /Al ³⁺

3. Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns of Bi³⁺ and Bi³⁺/Al³⁺ doped zeolites annealed at 1150 °C. The crystalline structure of Bi³⁺ singly doped sample keeps intact after thermal treatment. However, the amorphization takes place for Bi³⁺/Al³⁺ doped samples, although some weak diffraction peaks of zeolite phase can be observed. This indicates that the introduced bismuth and aluminum content existing in zeolite pores strongly affect the eutectic temperature of the samples.

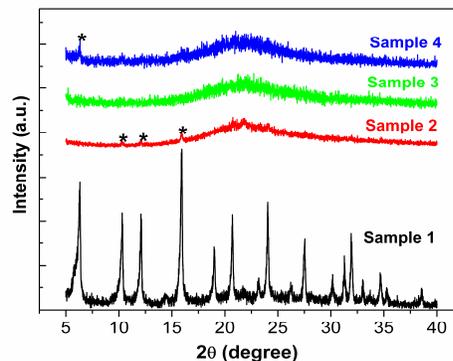


Fig. 1. XRD spectra of Bi³⁺ and Bi³⁺/Al³⁺ doped samples. The peaks denoted by the asterisks are ascribed to the reflections of zeolite phase.

Figure 2(a) displays a typical FE-SEM image of sample 3. The morphology and monodispersity of the annealed zeolites remain almost unchanged. The chemical composition of the above sample was analyzed by EDS as shown in Fig. 2(b), indicating that the particle is composed of Si, Al, O, and Bi. In combination with the corresponding XRD result, it is clear that the product is silica-alumina amorphous nanoparticles.

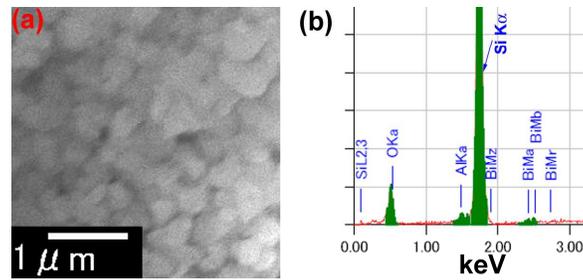


Fig. 2. (a) FE-SEM image of sample 3. (b) EDS of the above sample.

Figure 3 shows the NIR PL spectra of the samples. All samples show strong NIR emission from 930 to 1620 nm. It is noteworthy that the $\text{Bi}^{3+}/\text{Al}^{3+}$ doped samples show much stronger emission than Bi^{3+} singly doped one; sample 3 displays the strongest emission, which is about eight times stronger than that of sample 1. In Ref. 10, we proposed that subvalent Bi^+ ions is the NIR PL origin in doped zeolites: Bi^+ ions act as charge compensators of $[\text{AlO}_{4/2}]^-$ units. Thus, the existence of charge imbalance environment in host materials is requisite to the formation of infrared-active Bi^+ . It was revealed that the homogeneous binary $\text{SiO}_2\text{-Al}_2\text{O}_3$ glasses with 0.4 to up to 12.0 wt % Al_2O_3 contain a mixture of 4-, 5-, and 6-fold coordinated Al sites (Al^{IV} , Al^{V} , and Al^{VI}) [11]. The relative proportions of these sites are strongly dependent on composition with Al^{IV} being most dominant in glasses with <1 wt % Al_2O_3 . It was hypothesized that the tetrahedral $[\text{AlO}_{4/2}]^-$ units in glasses with <1 wt % Al_2O_3 are predominantly charge balanced by the formation of oxygen triclusters, and addition of either low field strength alkali ions such as K^+ or high field strength rare earth ions such as La^{3+} to these glasses results in charge balance and stabilization of Al^{IV} sites [11]. Therefore, it is reasonable to assume that more $[\text{AlO}_{4/2}]^-$ units will be formed after annealing when Al content was introduced into the matrix of zeolites, and more Bi^+ ions act as charge compensators of $[\text{AlO}_{4/2}]^-$ units. Owing to the extended nature of 6p orbitals of Bi^+ , the crystal field plays an important role in the luminescent properties. Thus, the host composition can affect the NIR emission as revealed before [2, 6]. For example, Meng et al. reported the peak position of the broadband infrared emission shifts from 1252 nm to 1300 nm with increasing BaO concentration from 20 mol% to 40 mol% in barium-aluminum-borate glasses. Interestingly, the shape of all spectra shown in Fig. 3 is nearly identical, indicating that Bi^+ ions has similar local environments in zeolites and their derived amorphous nanoparticles.

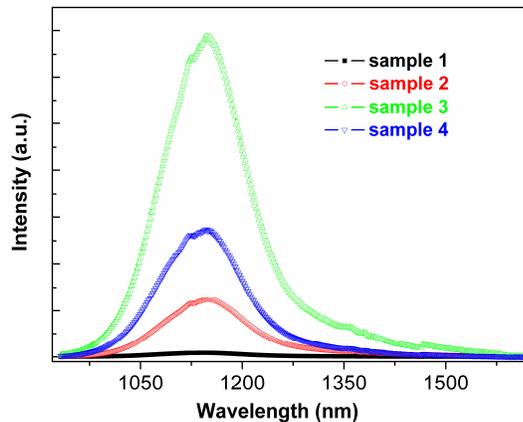


Fig. 3. PL spectra of the samples under the excitation of a 488 nm laser line. All samples were measured under the same condition.

To further know the PL enhancement mechanism, we measured the fluorescence decay curves of the samples (Fig. 4). The lifetimes of $\text{Bi}^{3+}/\text{Al}^{3+}$ doped samples are much longer than

that of bismuth doped one: with increasing aluminum and decreasing bismuth contents, the lifetime monotonously increases; sample 4 shows the longest 1/e lifetime of 695 μs , which is comparable to those reported in bulk glasses [1-5]. It appears that the changes of PL lifetimes are closely related to the structural evolution of zeolites. As revealed by the XRD result (Fig. 1), the microporous structure of the samples 2, 3 and 4 were destroyed, resulting in no room for the admission of water molecules. However, the crystalline structure of the sample 1 keeps well, thus water molecules have a chance to interact with active Bi^{3+} ions, leading to a much shorter lifetime and a fast part of the decay curve.

As is known, in the low-excitation regime the luminescence intensity I is proportional to $\sigma\Phi Nt/\tau_{rad}$, where σ is the excitation cross section, Φ the photon flux, N the content of optically active centres, τ the lifetime, and τ_{rad} the radiative lifetime. Assuming that τ_{rad} and σ of Bi^{3+} ions are same in these samples, the ratios of active Bi^{3+} ions in these samples can be estimated based on the following equation:

$$\frac{N_i}{N_1} = \frac{I_i \times \tau_1}{I_1 \times \tau_i} \quad (1)$$

where i is the sample no., N_i the number of Bi^{3+} ions in sample i , I the integrated PL intensity, and τ_i the measured 1/e lifetime. The calculated result is shown in Fig. 5. The number of Bi^{3+} ions in sample 3 is over twenty times more than that in sample 1. As shown in Table 1, the Al concentration monotonously increases from sample 1 to 4, while Bi concentration decreases. These results reveal that the increase of aluminum content is favorable to the formation of Bi active centres owing to the existence of more $[\text{AlO}_4/2]^-$ units. The number decrease of Bi^{3+} ions in sample 4 arises from the decreased bismuth concentration. These results clearly indicate that some bismuth in the samples is not infrared active, and the creation of a charge imbalance environment in the matrix is requisite to activate bismuth. The above result presents a feasible route to design high-efficient bismuth activated infrared luminescent nanoparticles.

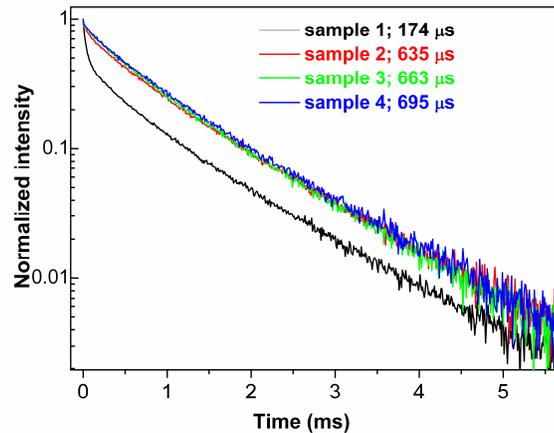


Fig. 4. Fluorescence decay curves of the samples. The detected wavelength is 1146 nm.

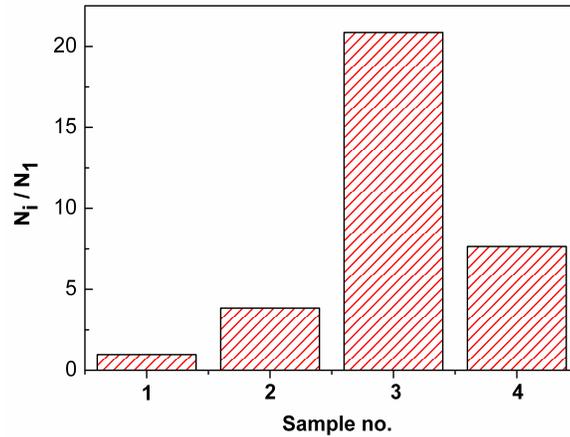


Fig. 5. The calculated ratios of active Bi^+ ions in these samples.

4. Conclusion

In summary, enhanced superbroadband near infrared emission has been realized in bismuth/aluminum doped high-silica zeolite derived nanoparticles. The emission covers the range of 930 ~ 1620 nm, with a lifetime of as long as 695 μs under the excitation of a 488 nm laser line. The results further reveal that the NIR emission should be from subvalent bismuth infrared active centre, i.e., Bi^+ , instead of others. The existence of a charge imbalance environment caused by $[\text{AlO}_{4/2}]^-$ units in host materials is requisite to the formation of infrared-active Bi^+ , which is the main reason for the enhanced emission in $\text{Bi}^{3+}/\text{Al}^{3+}$ doped high-silica zeolite derived nanoparticles. The finding may pave the way for the applications of these NIR luminescent nanoparticles as superbroadband near infrared nano optical sources.

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