

Superbroadband Near Infrared Emission from Bismuth Doped High-Silica Nanocrystalline Zeolites

Zhenhua Bai, Hong-Tao Sun, Yuji Miwa, Fumiaki Shimaoka, Minoru Fujii, Shinji Hayashi

*Department of Electrical and Electronic Engineering,
Graduate School of Engineering, Kobe University*

Efficient superbroadband near infrared luminescence can be realized in bismuth doped high-silica nanocrystalline zeolites. Bi ions not only act as superbroadband NIR luminescence centers, but also can act as blocks for selectively closing down the “in–out windows” of water molecules. This finding may pave the way for the applications of active ions doped porous materials in infrared photonics.

1. Introduction

In recent years, extensive studies on bismuth related superbroadband near-infrared 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.

In this Letter, we report efficient superbroadband near infrared emission in bismuth doped FAU-type nanocrystalline zeolites. This method consists of a simple ion-exchange process and subsequent high-temperature annealing under N_2 atmospheric condition. We also demonstrate that the emission intensity and luminescence lifetime can be easily tailored by changing the annealing temperature. Based on the measurement of steady-state and time-resolved

luminescence, we discussed the luminescence origin in detail.

2. Experimental

The H form of FAU-type zeolites were purchased from Tosoh Co. Japan (Zeolite Y, $\text{SiO}_2/\text{Al}_2\text{O}_3=200$, 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 NH_4 ions with Bi^{3+} ions. The products were removed by centrifugation, then washed with deionized water, and dried in air at 120 °C. The Bi^{3+} -exchanged zeolites were calcined at 1000 ~ 1300 °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, $\lambda=1.54056 \text{ \AA}$). 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. 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 light from an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) results of bismuth doped zeolites annealed at different temperatures. Zeolites structure keeps well even after thermal treatment at 1200 °C. Further increase of temperature results in the collapse of zeolites structure. Fig.2 displays the corresponding field emission scanning electron microscopy (FE-SEM) images of the samples. It reveals that the morphology and

monodispersity of the nanoparticles remain almost unchanged from 1000 to 1300 °C.

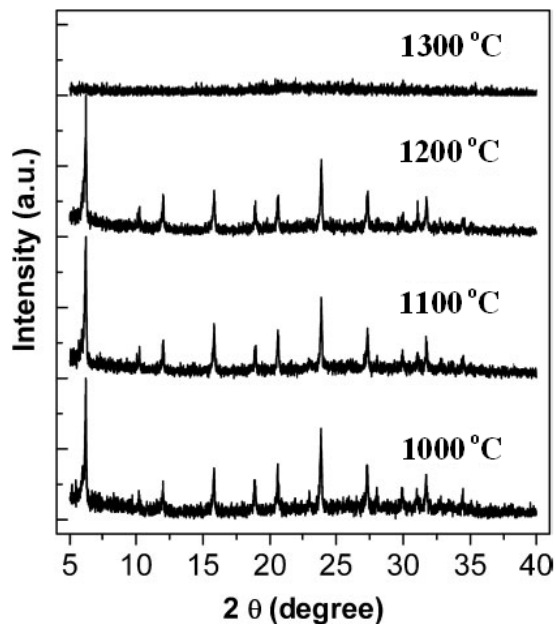


Fig. 1. XRD patterns of Bi doped zeolites annealed at different temperature in N₂ atmospheric condition.

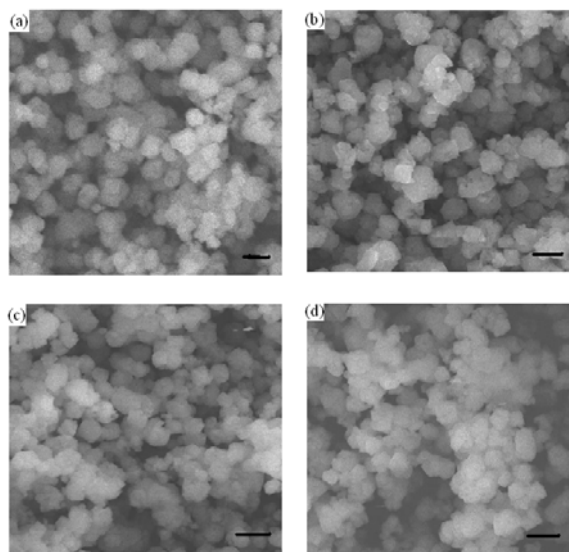


Fig. 2. FE-SEM images of zeolites annealed at a) 1000, b) 1100, c) 1200, and d) 1300 °C in N₂. Scale bars: 1 μm.

Fig. 3a shows the near infrared emission of bismuth doped zeolites annealed at different temperatures. All

samples show strong superbroadband NIR emission from 930 to 1470 nm with a full width at the half maximum (FWHM) of 152 nm under 488 nm excitation at a power of 3.2 mW. The peak wavelength is at 1146.3 nm. The shape of PL spectra of these samples is almost identical, indicating that the emission is from the same kind of active centres.

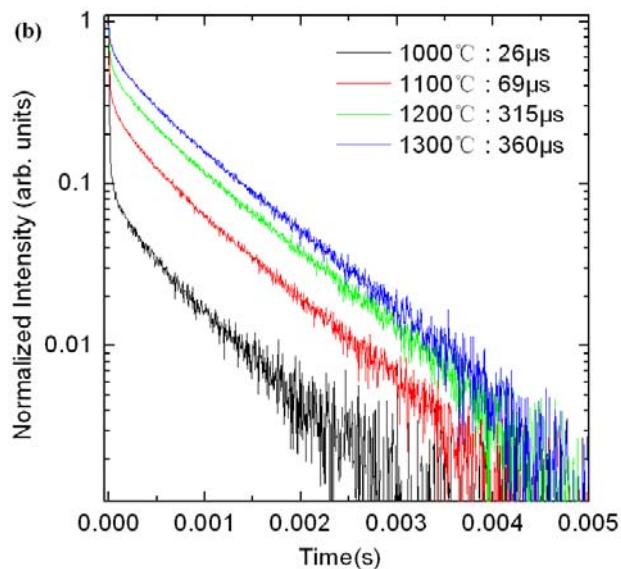
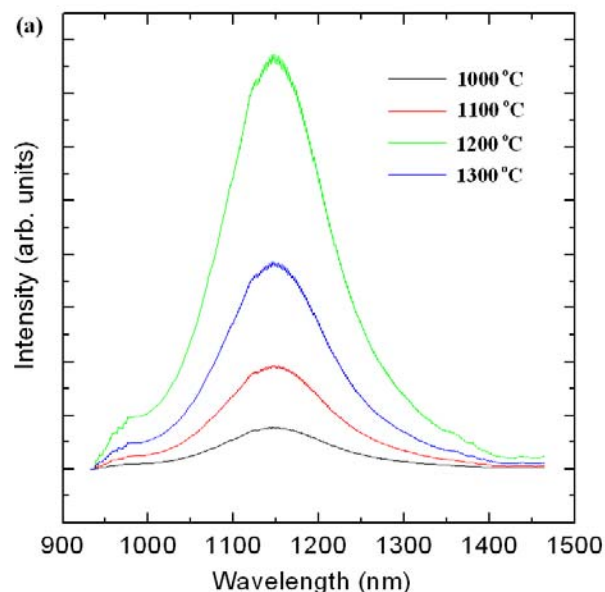


Fig. 3. (Color online) (a) Superbroadband luminescence spectra of the zeolites annealed at different temperatures in N₂ atmospheric condition, which were excited by a 488 nm line of an Ar⁺ laser. (b) Fluorescence decay curves of the above samples. The detected wavelength is 1146.3 nm and the excitation wavelength is 488 nm.

It is necessary to note that in zeolites without doping bismuth, we did not detect any near infrared emission. Thus, the emission is attributed to the bismuth-related active centres instead of intrinsic structural defects of zeolites. With increasing annealing temperature, the emission first reaches the maximum at 1200 °C and then decreases. As revealed by the XRD data, the zeolites structure was almost destroyed at 1300 °C. These results clearly indicate that amorphous matrix is not requisite to realize bismuth-related infrared emission. Fig. 3b displays the fluorescence decay curves of the samples, notably, which do not show single exponential decays. The 1/e lifetimes at 1146.3 nm are dependent on the annealing temperature. With increasing temperature, the lifetimes at 1146.3 nm monotonously increase. The lifetimes for the sample annealed at 1200 °C are 315 μ s, which is comparable to those of Bi-doped bulk multicomponent glasses [1, 2].

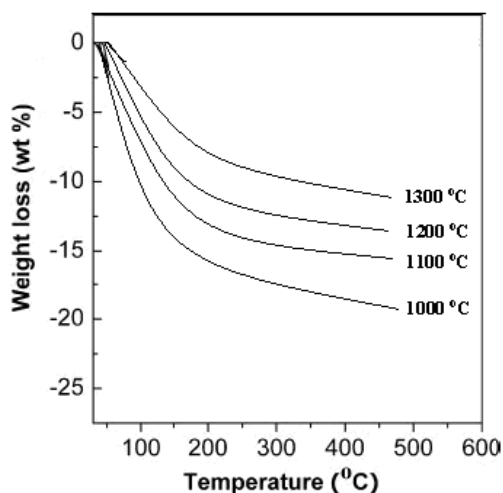


Fig. 4. TG analysis of Bi doped zeolites annealed at different temperature.

As for the origin of the bismuth-related infrared emission, different groups tentatively attributed it to the electronic transitions of bismuth ions with different valence states such as Bi^{5+} , Bi^+ , and Bi^{2+} , or of cluster of Bi atoms. For example, Fujimoto *et al* ascribed the absorption and emission bands of bismuth-doped silica glasses to the Bi^{5+} transitions between the ground state of $^1\text{S}_0$ and the excited states of $^3\text{D}_{3,2,1}$ and $^1\text{D}_2$ [1]. In contrast, Meng *et al* proposed that, most possibly, the emission arises from the electronic transitions of Bi^+ ions based on the systematical investigations of Bi doped glasses with different compositions and the well-known optical basicity theory proposed by J. A. Duffy [2, 10]. Very recently, Sharonov *et al* proposed that the point defect optical centres formed due to the

introduction of Bi is the luminescence origin based on their spectroscopic analysis of Bi, Pb, Sb, Sn, Te and In doped germanate glasses [11]. It is necessary to point out that, at present, in Pb, Sb, and Sn doped zeolites annealed at different temperatures and atmospheres (N_2 , Ar, and N_2/H_2), we did not observe any near infrared emission. Interestingly, we found that the near infrared luminescence in Bi doped zeolites is strongly dependent on the annealing atmosphere. Annealing the exchanged zeolites in an inert (N_2 or Ar) atmosphere is requisite to form high-efficient infrared active centres; in contrast, oxidizing (air) or reducing (N_2/H_2) atmosphere would destroy such centres. In Bi doped zeolites annealed in air, Bi^{3+} ions form in the matrix [12], while in N_2/H_2 atmosphere, bismuth metal preferentially forms [13]. In light of above results, we believe that high-valence (+3 or +5) and low-valence (0 or clusters) Bi is not the origin of NIR emission in Bi doped zeolites; the emission should be assigned to the electronic transition of subvalent Bi. Since Bi^{2+} ions are not infrared active, thus, most probably, Bi^+ is the near infrared luminescence origin: Bi^+ ions act as charge compensators of $[\text{AlO}_4]^-$ units.

It is noteworthy that zeolites are aluminosilicate molecular sieves with pores of molecular dimensions. Due to the microporosity, it is easy to absorb water in air [14]. Figure 4 shows that a large amount of water still contains in our samples. If the coordinated water strongly interact with active Bi ions, it is nearly impossible to show such long lifetimes. Based on the physical and chemical properties of bismuth compounds, we explain the effective near infrared emission as follows. When the exchanged zeolites were annealed in high temperatures, complicated bismuth-related redox reactions may take place [15]. The active Bi^+ and non-active Bi form simultaneously in this process. Owing to low melting points of bismuth compounds and high temperature (≥ 1000 °C) annealing, it has a chance to block the active Bi^+ in a water-free environment by 'using' non-active Bi liquid as a 'paste' when we suddenly cool down the annealed products. As is well known, FAU-type zeolites consist of three kinds of units, the supercages (or α -cages), the sodalite cages and the double 6-ring hexagonal prisms [16]. The pore openings of above three units is in sequence of α -cages>sodalite cages>hexagonal prisms. Therefore, it is reasonable to assume that the possibility of sealing the sodalite cages and hexagonal prisms is much larger than that of α -cages, and that active Bi^+ ions situate at different sites in the annealed products. In the low-excitation regime the luminescence intensity I is proportional to $\sigma\Phi N\tau/\tau_{\text{rad}}$, 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. As shown in Fig. 2, the luminescence intensity shows different annealing

temperature dependence in comparison with the lifetimes at 1146.3. It is hard to explain it by a model of single-type Bi active centres. We believe that the decrease of luminescence intensity at 1300 °C is due to the number decrease of Bi active centres contributing to it. It is necessary to point out that if the annealing temperature is ≤ 900 °C, no NIR emission can be observed in this kind of Bi doped zeolites. This also seems to evidence our above explanation.

4. Conclusion

Superbroadband near infrared emission peaked at 1146.3nm, with a FWHM >150 nm and a lifetime longer than 300 μ s, was observed in Bi doped high-silica nanocrystalline zeolites under the excitation of a 488 nm laser line. We assigned the emission to the electronic transition of Bi^{3+} . In view of their peculiar optical properties, we believe that these Bi-doped nanozeolites may find applications as superbroadband near infrared nano optical sources. This finding opens the door to realize infrared emission in Bi-doped nanosized materials.

1. Y. Fujimoto and M. Nakatsuka, "Optical amplification in bismuth-doped silica glass," *Appl. Phys. Lett.* **82**, 3325-3326 (2003).
2. X. Meng, J. Qiu, M. Peng, D. Chen, Q. Zhao, X. Jiang, and C. Zhu, "Infrared broadband emission of bismuth-doped barium-aluminum-borate glasses," *Opt. Express* **13**, 1635-1642 (2005).
3. V. V. Dvoyrin, V. M. Mashinsky, L. I. Bulatov, I. A. Bufetov, A. V. Shubin, M. A. Melkumov, E. F. Kustov, E. M. Dianov, A. A. Umnikov, V. F. Khopin, M. V. Yashkov, and A. N. Guryanov, "Bismuth doped-glass optical fibers-a new active medium for lasers and amplifiers," *Opt. Lett.* **31**, 2966-2968 (2006).
4. Y. Arai, T. Suzuki, Y. Ohishi, S. Morimoto, and S. Khonthon, "Ultrabroadband near-infrared emission from a colorless bismuth-doped glass," *Appl. Phys. Lett.* **90**, 261110-1-3 (2007).
5. V. O. Sokolov, V. G. Plotnichenko, and E. M. Dianov, "Origin of broadband near-infrared luminescence in bismuth-doped glasses," *Opt. Lett.* **33**, 1488-1490 (2008).
6. Q. Qian, Q. Y. Zhang, G. F. Yang, Z. M. Yang, and Z. H. Jiang, "Enhanced broadband near-infrared emission from Bi-doped glasses by codoping with metal oxides," *J. Appl. Phys.* **104**, 043518-1-3 (2008).
7. Okhrimchuk, L. Butvina, E. Dianov, N. Lichkova, V. Zagorodnev, and K. Boldyrev, "Near-infrared luminescence of RbPb_2Cl_5 : Bi crystals," *Opt. Lett.* **33**, 2182-2184 (2008).
8. P. Li, X. H. Sun, N. B. Wong, C. S. Lee, S. T. Lee, and B. Teo, "Ultrafine and uniform silicon nanowires grown with zeolites," *Chem. Phys. Lett.* **365**, 22-26 (2002).
9. M. Ryo, Y. Wada, T. Okubo, T. Nakazawa, Y. Hasegawa, and S. Yanagida, "Spectroscopic study on strongly luminescent Nd(III) exchanged zeolite: TMA+-containing FAU type zeolite as a suitable host for ship-in-bottle synthesis," *J. Mater. Chem.* **12**, 1748-1753 (2002).
10. J. A. Duffy, "Redox equilibria of glass," *J. Non-Cryst. Solids* **196**, 45-50 (1996).
11. M. Sharonov, A. Bykov, V. Petricevic, and R. Alfano, "Spectroscopic study of optical centers formed in Bi, Pb, Sb, Sn, Te and In-doped germanate glasses," *Optics Letters* **33**, 2131-2133 (2008).
12. D. Dumitriu, R. Bârjega, L. Frunza, D. Macovei, T. Hu, Y. Xie, V.I. Pârvulescu, and S. Kaliaguine, "BiOx clusters occluded in a ZSM-5 matrix: preparation, characterization, and catalytic behavior in liquid-phase oxidation of hydrocarbons," *Journal of Catalysis* **219**, 337-351(2003).
13. S.Korenev, I. Novoselov, A. Galitskii, Y. Vasil'ev, "Gravimetric determination of bismuth in high-purity Bi_2O_3 ," *Industrial Laboratory* **66**, 511-512 (2000).
14. A. Monguzzi, G. Macchi, F. Meinardi, R. Tubino, M. Burger, and G. Calzaferri, "Sensitized near infrared emission from lanthanide-exchanged zeolites," *Appl. Phys. Lett.* **92**, 123301-1-123301-3 (2008).
15. J. Ren, L. Yang, J. Qiu, D. Chen, X. Jiang, and C. Zhu, "Effect of various alkaline-earth metal oxides on the broadband infrared luminescence from bismuth-doped silicate glasses," *Solid State Communications* **140**, 38-41 (2006).
16. E.M. Dianov, V.V. Dvoyrin, V.M. Mashinsky, A.A. Umnikov, M.V.Yashkov, A.N.Guryanov, "CW bismuth fiber laser", *Quant. Electron.*, **35**, 1083-1084 (2005).