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Effect of doping concentration on broadband near-infrared emission of Bi doped zeolites

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ABSTRACT

A series of Bi doped zeolites are prepared by an ion-exchange process by changing doping concentration in a wide range, and the optical properties are investigated. The near-infrared photoluminescence (PL) intensity, full width at half maximum and decay time depend strongly on Bi doping concentration. The PL intensity increases 178 times when the concentration is changed from 0.3 to 1.5 at. %. At the same time, the lifetime increases from 83 to 527 μs. The results prove the model that doped Bi acts not only as optically active centers, but also as pore-sealing substances to isolate the centers. The comparison of PL and Raman data suggests that in addition to previously proposed Bi_2O_3, other Bi-related materials, probably Bi metal, play an important role to isolate the active centers.

1. Introduction

With the rapid development of optical telecommunication, there exists an urgent requirement to develop broadband fiber amplifiers and laser sources to achieve more efficient wavelength division multiplexing transmission network with higher capacity and faster bit rate. Recently, the telecommunication transmission window has been extended to the range from 1.2 to 1.7 μm by the elimination of OH in silica fibers. As a result, exploring a new luminescent material which can cover the whole telecommunication window has attracted great attention [1–8]. More recently, Fujimoto and Nakatsuka reported a broadband near-infrared (NIR) emission from Bi-doped silica glass and realized its optical amplification at 1300 with 800 nm excitation [1,2]. Subsequently, the broadband NIR emissions of Bi were investigated in different host materials, such as glasses [3,4], crystals [5,6], and zeolites [7,8].

Zeolites are microporous crystalline aluminosilicates with nanosized pores. Their framework is composed of SiO_4 and AlO_4 tetrahedra units by sharing oxygen between every two consecutive units, and cations located inside channels or cavities to balance negative charges in the framework. For a long time, zeolites played indispensable roles in many technological and economical applications, such as catalysis, ion exchange, and separations [9,10]. Recently, zeolites acting as host materials of optically active guests have attracted much attention for constructing novel materials designed at nanosized levels, because of their low-frequency vibrational framework, regularly spaced nanochannels and nanopores, and inexpensive price [11–27]. At present, visible luminescence with very high efficiencies from rare-earth-functionalized zeolites has been reported [11,12]. However, it is not easy to observe efficient NIR emission in zeolites, due to the strong non-radiative relaxation of the excited energies by water molecules within the pores of the zeolites host [13,14]. Until now, several strategies have been reported to overcome this difficulty [7,15–19]. Very recently, Sun et al. [7] reported efficient broadband NIR luminescence from Bi doped zeolites. They proposed that effective isolation of Bi-related active centers from environment by Bi_2O_3 agglomerates results in the efficient NIR luminescence [27]. In this process, the Bi concentration is a very important parameter to achieve the maximum luminescence efficiency because doped Bi acts not only as NIR luminescence centers but also as pore-sealing substances. However, the effect of doping concentration on optical properties in Bi doped zeolites has not been investigated in detail.

In this work, we investigate the optical properties of Bi doped zeolites by changing doping concentration in a very wide range. The measurement results show that NIR photoluminescence (PL) intensity, full width at half maximum (FWHM) and decay time are strongly dependent on Bi concentration in zeolites. Highly efficient NIR emission from Bi-related active centers can be realized by increasing Bi concentration to 1.2 at. %, and further increase causes the shortening of lifetime. It is also proposed that Bi_2O_3 and bis-

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muth metal agglomerates are formed in zeolites, and separate Bi-related active centers from quenchers.

2. Experimental

2.1. Sample preparation

The samples used in this study were synthesized by an ion-exchange method. The NH_4 form of faujasite (FAU) type zeolite was purchased from Tosoh Co. Japan (Zeolite Y, $SiO_2/Al_2O_3 = 7$, grain size 700–1000 nm). Zeolites were stirred in a 10–80 mM aqueous solution of Bi^{3+} prepared from $Bi(NO_3)_3{\cdot}5H_2O$ for 24 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 doped zeolites were calcined at 900 °C for 1 h in N_2 atmospheric condition. All samples were exposed to the laboratory atmosphere prior to measurements.

2.2. Characterization

The prepared products were characterized by an X-ray diffractometer (Rigaku-TTR/S2, $\lambda = 1.54056$ Å), and the crystallinity of all samples is estimated from the ratio of the sums of the intensities of the peaks (1 1 1), (3 1 1), (3 3 1), (5 1 1), (4 4 0), (5 3 3), and (6 4 2) of the doped zeolites and the undoped-zeolites, by following a usual procedure [28,29]. Bi concentration was determined by energy-dispersive X-ray spectroscopy (EDS). Hereafter, the samples were denoted as Bi-*X*, where *X* is bismuth atomic concentrations in the final products. PL measurements were carried out with the excitation of a 488 nm line from an Ar^+ laser and a 355 nm line from a He–Cd laser. The signal was analyzed by a single grating monochromator and detected by liquid-nitrogen-cooled InGaAs and CCD detectors. PL excitation spectrum was obtained by a NIR PL spectrophotometer (Bunkoh-Keiki Co. Ltd., Tokyo, Japan) equipped with an InGaAs detector. The absorption spectrum was measured by a Jasco V-570 UV–Vis-NIR spectrophotometer. 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 decay time measurements was 488 nm light from an optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser (pulse width 5 ns, repetition frequency 20 Hz). Raman spectra were recorded by using a SPEX 1877 triple spectrometer under the excitation of a 514.5 nm line from the Ar^+ laser. All the measurements were carried out at room temperature.

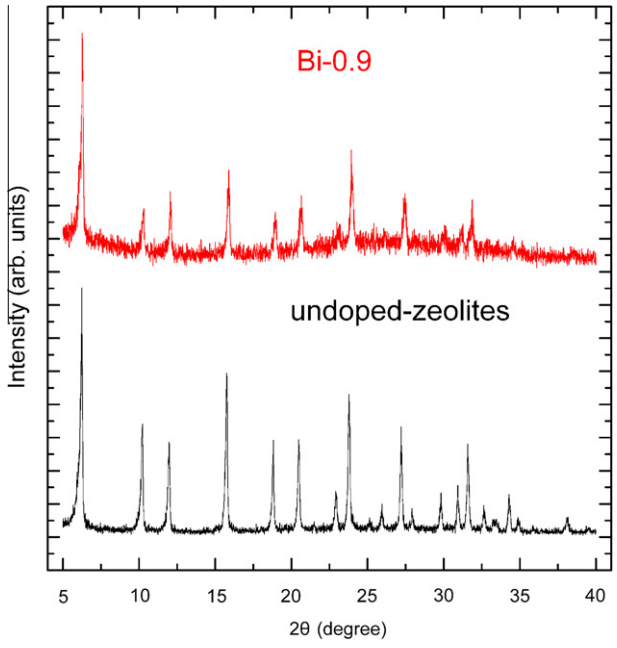

Fig. 1. X-ray diffraction patterns of undoped-zeolites and Bi doped zeolites (Bi-0.9).

3. Results and discussion

The color of the powder samples turned gradually from white to shallow pink with increasing concentration of Bi ions. Fig. 1 shows the XRD patterns of undoped-zeolites and Bi doped zeolites (Bi-0.9). The comparison of two spectra indicates that no new diffraction peak develops after doping and thermal treatment. However, a broad background appears and the peak intensity decreases in Bi doped zeolites. The crystallinity of all samples is calculated to be 92% (Bi-0.3), 78% (Bi-0.6), 67% (Bi-0.9), 61% (Bi-1.2), and 54% (Bi-1.5). The results reveal a decreasing trend of crystallinity as the

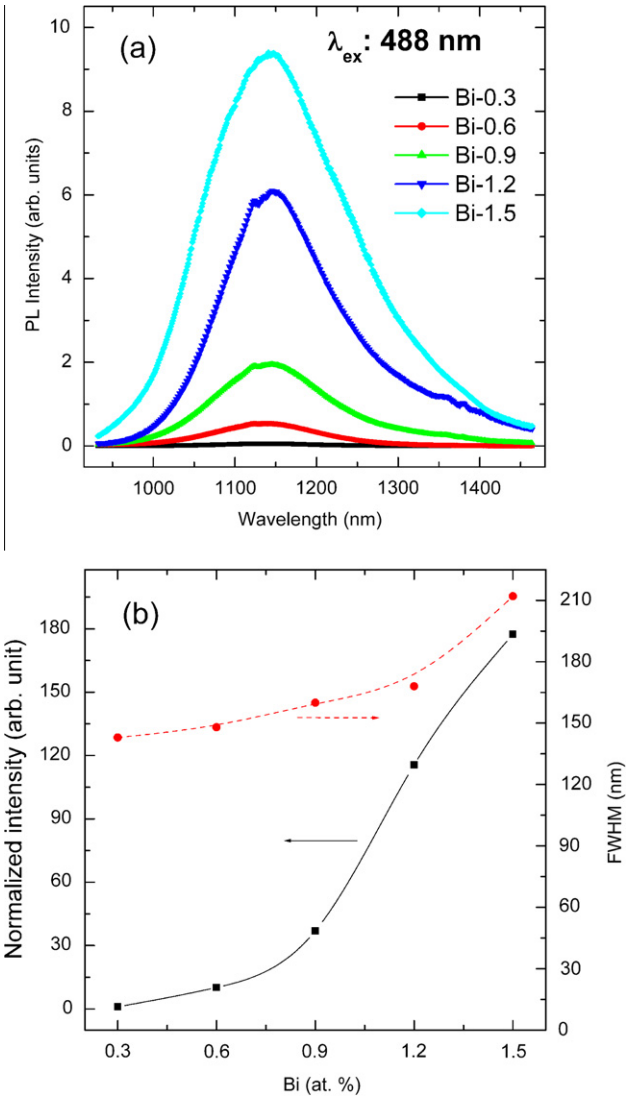

Fig. 2. (a) PL spectra of Bi doped zeolites in the NIR range, excited at 488 nm. (b) The normalized intensity at 1145 nm (left scale) and full width at half maximum (right scale) as a function of Bi concentration. Note that the arrows were drawn for guiding the eye.