Supporting Information

Synchrotron X-ray, Photoluminescence and Quantum Chemistry Studies of Bismuth Embedded Dehydrated Zeolite Y

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Experimental details

Synthesis of optically active bismuth embedded zeolite Y:

The Na-Y zeolites were purchased from Tosoh Co. Japan. Zeolites was stirred in a 2 mM aqueous solution of Bi^{3+} prepared from $Bi(NO_3)_3 \cdot 5H_2O$ (Wako Pure Chemical Industries, Ltd., 99.9%) at room temperature for 24 h to exchange the Na ions with Bi^{3+} ions. The products were removed by centrifugation, then thoroughly washed with deionized water, and dried in air at 120 ^oC. Ultrapure water (18.2 MΩ/cm) was used throughout the work. The obtained powders were first put into a 5 mL flask with an adapter, and then inserted into the chamber of a vacuum furnace. The sample was thermally treated from room temperature to 400 ^oC at a rate of 10 ^oC/min, and kept at 400 ^oC and 6 x 10^{-5} Pa for 24 h. The dehydrated powder was allowed to cool to room temperature and was stored in the glovebox (< 2 ppm H_2O; < 0.1 ppm O_2) for the following measurements.

ICP-OES, thermogravimetric (TG) and diffuse reflectance spectrum measurements:

The atomic ratio of Bi:Na:Al:Si for the annealed zeolites was determined to be 8.5 : 26.6 : 53.5 : 138.5 by the analysis of inductively coupled plasma-optical emission spectrometer (ICP-OES: IRIS Advantage, Nippon Jarrell-Ash, Yokohama, Japan). TG analysis of the samples fully exposed in air over 24 h was taken with the Rigaku Thermo Plus TG-DTA series (TG 8120). Diffuse reflectance spectrum of the products were measured by a UV-vis-NIR spectroscope (V-570, JASCO, Japan) equipped with an integrating sphere.

Synchrotron X-ray, steady-state and time-resolved photoluminescence measurements:

To overcome the influence of water and oxygen on bismuth active centers in the zeolite framework, the loading of annealed zeolites into capillaries was carried out in a high-purity N_2 filled glovebox (< 2 ppm H_2O; < 0.1 ppm O_2). We employed high-resolution synchrotron XRD at the BL15XU NIMS beam line of SPring-8 to obtain high-quality diffraction patterns. All the samples for XRD were sealed into Lindemann glass capillaries with an inner diameter of 0.3 mm.

The capillary was rotated during the measurement to reduce the preferred orientation effect and to average the intensity. X-ray wavelength used is 0.65297 Å. After XRD measurement, the same sample was further used for the following luminescence measurements. Steady-state luminescence measurements were carried out at room temperature with the excitation of 488 nm line of an Ar^+ laser and 786 nm light of an laser diode. The excitation beam was focused on the silica capillary loaded with annealed zeolites after XRD measurement, and the signal was analyzed by a single grating monochromator and detected by a liquid-nitrogen-cooled InGaAs detector**.** The spectral response of the detection system was corrected by the reference spectrum of a standard tungsten lamp. Time-resolved PL measurements were performed by detecting the modulated luminescence signal at 1150 nm with a photomultiplier tube (Hamamatsu, R5509-72), and then analyzing the signal with a photon-counting multichannel scaler. The time resolution is 80 ns. The excitation source for the time-resolved PL measurements was 488 nm light (pulse width: 5nsec; frequency: 20Hz) from an optical parametric oscillator pumped by the third harmonic of a Nd:YAG laser. All the measurements were taken at room temperature.

Crystal structure refinement of high-resolution synchrotron XRD by Rietveld method:

First, it is necessary to note that no patterns assigned to bismuth metal or oxides were observed in the XRD spectrum. The Rietveld refinement has been performed using the software package GSAS (General Structure Analysis System). The refinement has been done in two sequential steps. We first try to refine the structure starting from the framework atoms without extra-framework cations, using a starting .cif file as shown in the IZA-SC website (http://izasc-mirror.la.asu.edu/fmi/xsl/IZA-SC/ftc_fw.xsl?-db=Atlas_main&-lay= fw&-max=25&STC=FAU&-find). After this step, we could find three major peaks at (0.0750, 0.0750, 0.0750), (0, 0, 0) and (0.0488, 0.0488, 0.0488) from the difference Fourier map. It is noteworthy that no peaks at sites SII, SII', SIII in the difference Fourier map can be found, suggesting no Na or Bi locates in these sites. In the second step, cations were introduced into the model. From ICP-OES result, it is clear that lots of Na still exists in the exchanged sample. Considering that cations in site SI is rather hard to be exchanged totally, we located partial Na in site SI at the beginning, while the rest Na in (0.0488, 0.0488, 0.0488). The Bi cation was arranged at (0.0750,

0.0750, 0.0750) owing to the following reasons: (1) the R_{ho} of this peak in the difference Fourier map is much larger than those of the other two; (2) Bi has a very high Z value. After loading all atoms, we further refined the structure. The quality of the Rietveld refinements is confirmed by the low values of R_{wp} and R_p, which are 3.14% and 2.01%, respectively. The refined cell parameter is a= 24.60237(14) Å [V = 14891.2(2) Å^3, Fd-3m].

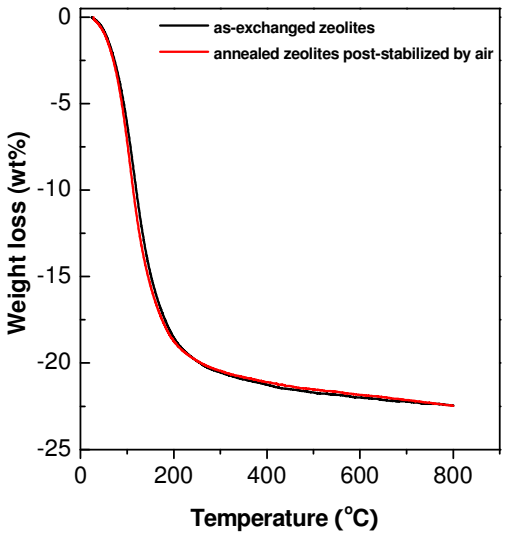

Figure S1. TG curves of the as-exchanged and annealed zeolites post-stabilized by air, with a stoichiometry $Bi_{8.5}Na_{26.6}$ $[Al_{53.5}Si_{138.5}O_{384}]$ per unit cell. At 800 °C, the weight losses of the zeolites as-exchanged and annealed are 24.46%, suggesting that the composition of the as-exchanged zeolites is $Bi_{8.5}Na_{26.6}$ $[Al_{53.5}Si_{138.5}O_{384}]\cdot 249.4H_2O$.

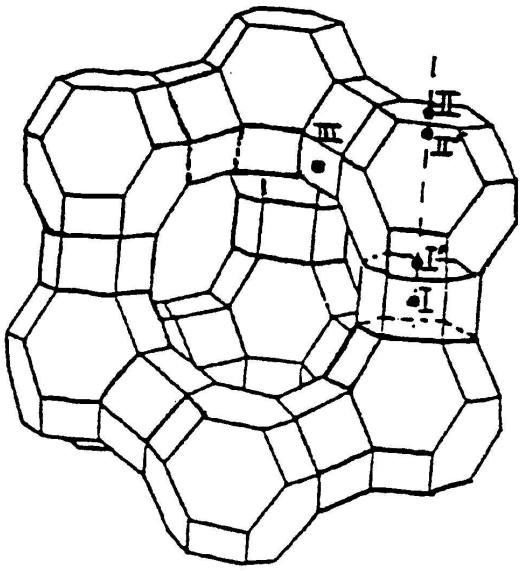

Figure S2. Unit cell of zeolite Y including cation sites.

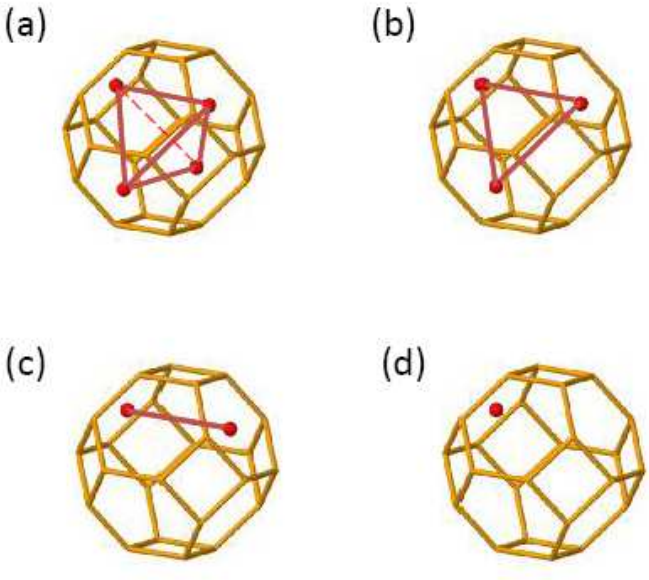

Figure S3. The possible distributions of Bi in sodalite cage of zeolite Y. (a), (b), (c) and (d) represent that four, three, two and one Bi situate at site I′ in one sodalite cage, respectively.

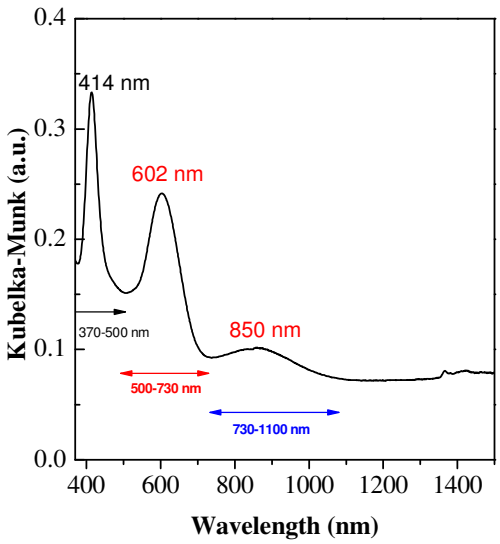

Figure S4. The experimental diffuse reflectance spectrum of as-annealed dehydrated zeolites.

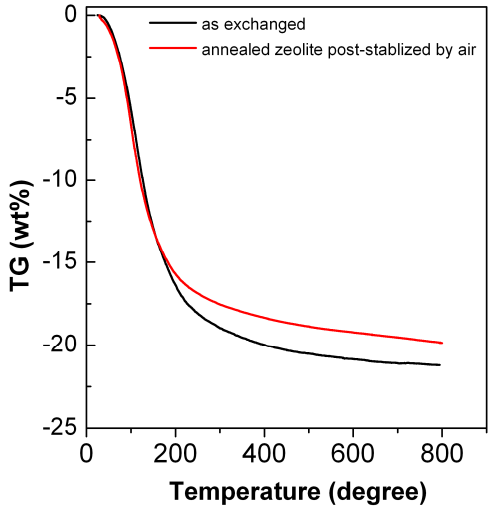

Figure S5. TG curves of the as-exchanged and annealed zeolites post-stabilized by air, with a stoichiometry $Bi_{13.3}Na_{15.2}[Al_{53.5}Si_{138.5}O_{384}]$ per unit cell. The annealed sample was prepared according to the same procedure with that of $Bi_{8.5}Na_{26.6}[Al_{53.5}Si_{138.5}O_{384}]$ sample. Note that after annealing, the water content becomes less, suggesting that partial pores of zeolites were blocked or collapsed owing to the formation of relatively large amount of subvalent Bi. This may arise from the lowing melting point of bismuth (for instance, Bi metal has a melting point of 271.5 °C).

Table S1: Atomic Parameters Obtained by the Rietveld Refinement

Atom	Wyckoff site	x	y	z	U_{iso}(Å^2)	Occupancy factor	Number of atoms per unit cell
Si	192i	0.94607(8)	0.12916(9)	0.03596(10)	0.0260(5)	0.721	138.43
Al	192i	0.94607(8)	0.12916(9)	0.03596(10)	0.0260(5)	0.279	53.57
O1	96h	0.89155(16)	0.10845(16)	0.00000(0)	0.0692(35)	1	96
O2	96g	0.96623(21)	0.07788(16)	0.07788(16)	0.0110(22)	1	96
O3	96g	1.00208(15)	0.14296(22)	1.00208(15)	0.0199(26)	1	96
O4	96g	0.92845(22)	0.18069(18)	0.06931(18)	0.0285(27)	1	96
S_I (Na)	16d	0	0	0	0.091(15)	0.433(9)	6.9(1)
$S_{I'}$ (Na)	32e	0.04883(29)	0.04883(29)	0.04883(29)	0.051(6)	0.597(5)	19.1(2)
$S_{I'}$ (Bi)	32e	0.07940(9)	0.07940(9)	0.07940(9)	0.0949(16)	0.263(1)	8.4(0)

Table S2: Selected Interatomic Distance (Å) and Angles (deg) (T stands for Si or Al)

Distances	Å	**Angles**	degree
T-O1	1.6856(29)	O1-T-O2	109.00(25)
T-O2	1.7034(27)	O1-T-O3	117.56(23)
T-O3	1.6459(27)	O1-T-O4	107.37(28)
T-O4	1.5711(30)	O2-T-O3	102.45(27)
mean	1.6515	O2-T-O4	111.22(32)
		O3-T-O4	109.21(31)
Na1-O2	2.834(6)	***mean***	109.45
Na2-O2	2.270(6)		
Na2-O3	2.830(5)	T-O1-T	139.2(4)
Bi-O2	2.785(6)	T-O2-T	144.3(4)
Bi-Bi	3.173(7)	T-O3-T	143.7(4)
		T-O4-T	140.1(4)
		mean	141.8
		Bi-Bi-Bi	60

Table S3: The calculated SPIN-POLARIZED excitation energies, oscillator strengths, and lifetimes for Bi_4^{4+}. Note that the transitions are Singlet to Triplet (i.e., forbidden-like transitions) in the case that the oscillator strength is zero.

Transitions	**Excitation energy/eV**	**Wavelength/nm**	**oscillator strength**	**Lifetime/second**	**Symmetry**
1	0.98006	1265.229	2.31E-34		T1
2	1.00272	1236.636	0.00E+00		E
3	1.28141	967.684	8.09E-04	1.74E-05	T2
4	1.95832	633.1958	0.00E+00		E
5	1.96803	630.0717	1.90E-34		T1
6	1.98081	626.0065	6.12E-04	9.60E-06	T2
7	2.08997	593.31	8.08E-34		T1
8	2.14017	579.3932	2.08E-33		A2
9	2.23996	553.5813	0.00E+00		A1
10	2.26319	547.8992	8.22E-04	5.47E-06	T2

Table S4: The calculated SPIN-POLARIZED excitation energies, oscillator strengths, and lifetimes for Bi_3^{3+}. Note that the transitions are Singlet to Triplet (i.e., forbidden-like transitions) in the case that the oscillator strength is zero.

Transitions	Excitation energy/eV	Wavelength/nm	oscillator strength	lifetime/s	Symmetry
1	0.8259	1501.392	0		A2'
2	0.94347	1314.297	0		E"
3	1.1115	1115.61	0		A1'
4	1.60233	773.873	0		E"
5	1.72421	719.1699	2.94E-04	2.64E-05	A2"
6	1.72613	718.37	1.33E-04	5.80E-05	E'
7	1.73294	715.547	8.32E-60		A1"
8	1.93777	639.9108	3.92E-60		A1"
9	1.97079	629.1893	2.56E-04	2.32E-05	E'
10	2.26153	548.3014	1.74E-03	2.59E-06	E'

Table S5: The calculated SPIN-POLARIZED excitation energies, oscillator strengths, and lifetimes for Bi_2^{2+}. Note that the transitions are Singlet to Triplet (i.e., forbidden-like transitions) in the case that the oscillator strength is zero.

Transitions	Excitation energy/eV	Wavelength/nm	oscillator strength	lifetime/s	Symmetry
1	1.22455	1012.617	0		Pi.g
2	1.36E+00	914.5217	5.73E-46		S-.u
3	1.54E+00	807.0657	1.21E-05	8.08E-04	Pi.u
4	1.72E+00	720.8464	0.00E+00		De.g
5	2.01E+00	618.4014	1.58E-04	3.64E-05	Pi.u
6	2.12E+00	583.6338	0.00E+00		S-.g
7	2.14E+00	580.4673	0.00E+00		De.u
8	2.38E+00	520.2826	0.00E+00		Pi.g
9	2.42E+00	513.3109	0.00E+00		S+.g
10	2.57E+00	481.6656	6.02E-02	5.78E-08	S+.u