Location of Tb(III) ions in Na-Y zeolite determined by luminescence spectroscopy

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The variation of the cation location and occupancy at different sites in TbNa-Y zeolites as a function of treatment temperature is monitored by luminescence spectroscopy. It is found that the spectral changes caused by thermal treatments can be qualitatively rationalized in terms of the site symmetry around the Tb(III) ion. The luminescence results demonstrate that most of the Tb(III) ions exchanged into supercages of the zeolite migrate first to sodalite cages at temperatures lower than 473 K and then migrate to hexagonal prisms between 473 and 523 K.

Keywords: location of Tb(III) ions in Na-Y; luminescence spectroscopy; thermal treatments; migration

1. Introduction

In view of zeolite catalysis, detailed information of the distribution of rare-earth ions in zeolites is of practical importance because both thermal stability and catalytic performance of zeolites are dramatically enhanced by ion exchange with rare-earth ions [1]. Most of the cation location data which are available in the literature have been obtained from single crystal and powder X-ray diffraction methods, although the determination of the cation distribution in zeolites includes a number of analytical techniques [2–9]. A serious problem encountered in using diffraction methods for the investigation of the cation in zeolites is that only the stationary cations can be located. More than 50% of the cations cannot often be located for hydrated zeolites by diffraction methods since some cations in zeolites are very mobile, especially, in the presence of water. In addition, such experiments have not been done for a wide variety of rare-earth-ion-exchanged zeolites. The

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chemical shift and line shape of the high resolution solid state ^{23}Na and ^{29}Si NMR spectra for LaNa-Y zeolites are reported to be dependent on the degree of hydration as well as the location of cations [7–9]. However, the results from NMR measurements do not give direct information on the location of rare-earth ions in zeolites since the nuclei investigated are not NMR active.

The purpose of this work is to evaluate the applicability of luminescence spectroscopy in monitoring the thermal effects on the distribution of rare-earth ions in zeolites. Luminescence methods have been used to study the effects of thermal or chemical treatments on the physicochemical properties of rare-earth ions in zeolites such as changes in coordination environment [10,11], or oxidation states [12,13]. However, no detailed luminescence studies focused on the thermal effects on the intrazeolitic distribution of rare-earth ions have been reported. Here we present the results obtained from the luminescence spectra of TbNa-Y zeolites treated at different temperatures. Most of the dehydrated rare-earth-ion-exchanged zeolites show luminescence spectra that are extremely broadened with respect to hydrated samples [14]. Prior to luminescence measurements, therefore, all the samples discussed in the work were fully rehydrated after thermal treatments at desired temperatures. The Tb(III) ion was chosen as a luminescent probe since its oxidation state in zeolites remains unchanged by thermal treatments at high temperatures [14].

2. Experimental

Na-Y was obtained from Aldrich. The Na-Y was refluxed twice in 1.0 M $NaNO_3$ solutions overnight in order to ensure that the sample was in its complete Na form. TbNa-Y was prepared by ion exchange of Na-Y at room temperature in 0.05 M $Tb(NO_3)_3$ solutions for 24 h. The pH of the $Tb(NO_3)_3$ solutions containing zeolite powder was 6.0. Ion exchange was done at 0.01 g ml^{-1}. After heating under the flowing N_2 at a given temperature for 6 h, the TbNa-Y sample was fully rehydrated over saturated NH_4Cl solution at room temperature for 2 d.

X-ray powder diffraction patterns of the samples were recorded on a Rigaku D/Max-IIA diffractometer. Chemical analysis was performed by a Jarrell-Ash Polyscan 61E inductively coupled plasma (ICP) spectrometer. The water contents in TbNa-Y samples rehydrated after thermal treatments at different temperatures were determined by a Dupont 950 thermogravimetric analyzer. The nitrogen BET surface areas were measured on a Micromeritics ASAP 2000 analyzer. Excitation and emission spectra were obtained at room temperature using a home-built instrument. A 150 W Xe arc lamp with an Oriel 1/8 m monochromator was used as an excitation source. The luminescence signal was detected using an Oriel 1/8 m monochromator and a Hamamatsu R928 photomultiplier tube. All the excitation and emission spectra were corrected for the optical system response function.

3. Results and discussion

3.1. PHYSICAL PROPERTIES

X-ray diffraction patterns of TbNa-Y samples show that all the characteristic peaks of Na-Y remain intact after thermal treatment and rehydration steps. Bulk chemical analysis reveals that the Si/Al ratio of Na-Y and the percentage of Na(I) exchanged with Tb(III) are 2.52 and 74%, respectively. The color of TbNa-Y zeolites after thermal treatments up to 773 K remains white like Na-Y. The water contents and nitrogen BET surface areas of TbNa-Y samples studied in this work are listed in table 1. The TbNa-Y dried at room temperature has about 10% more water molecules per unit cell than Na-Y. Upon heat treatments the number of water molecules per unit cell for TbNa-Y samples decreases. However, it is interesting to note that the value is almost constant for the samples treated at 423–573 K. No significant differences in the BET surface area of TbNa-Y samples treated at temperatures higher than 523 K indicate that the crystallinity of TbNa-Y is not lowered by thermal treatments.

3.2. EMISSION SPECTRA

Fig. 1 shows changes in the emission spectra of TbNa-Y samples, which are caused by thermal treatments at different temperatures. All the spectra in fig. 1 consist of emission bands due to the $^5D_4 \rightarrow {}^7F_j$ transitions of the Tb(III) ion. The emission band intensities of the TbNa-Y samples are dependent on the excitation wavelength, but their band positions and shapes are not. Fig. 1a was obtained from unheated TbNa-Y. This spectrum gives four emission bands at 491, 547, 587 and 624 nm. These values are in agreement with those reported by Tanguay and Suib [14].

Table 1
The water content and BET surface area of TbNa-Y zeolites

Sample[a]	Treatment temperature (K)	g H_2O/ g dry solid[b]	No. of H_2O molecules/u.c.	BET surface area[c] (m^2/g)
Na-Y	–	0.329	232	882
TbNa-Y	300	0.341	264	–
	373	0.318	246	–
	423	0.300	232	–
	473	0.299	231	–
	523	0.301	233	732
	573	0.297	230	736
	673	0.283	219	723
	773	0.286	221	760

[a] Unit cell composition: Na-Y, $Na_{54.5}Al_{54.5}Si_{137.5}O_{384}$; TbNa-Y, $Tb_{13.5}Na_{14.0}Al_{54.5}Si_{137.5}O_{384}$.

[b] Calculated from TGA.

[c] BET surface areas calculated from nitrogen adsorption data.

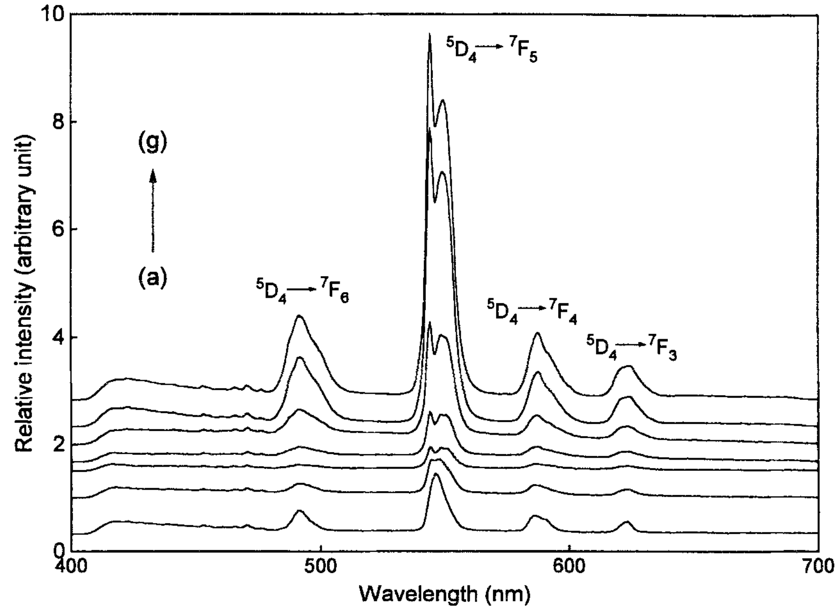

Fig. 1. Emission spectra of TbNa-Y zeolites treated at 300 (a), 373 (b), 423 (c), 523 (d), 573 (e), 673 (f), and 773 K (g). The excitation wavelength is 232 nm.

The evacuation of unheated TbNa-Y at room temperature under the vacuum ($< 10^{-4}$ Torr) overnight yields the spectrum that is broadened as compared to that of the hydrated sample. However, the subsequent rehydration of this sample at ambient conditions restores it to its original state. The emission spectrum of unheated TbNa-Y is also quite similar to that obtained from 0.05 M $Tb(NO_3)_3$ solution. Rare-earth ions such as Eu(III) or Tb(III) are known to be surrounded by eight or nine water molecules in aqueous solution [15,16]. Re-exchange of unheated TbNa-Y with Na(I) yields a significant decrease in the band intensity, indicating that the Tb(III) ions are exclusively placed at exchangeable sites in supercages. Suib et al. [17] have observed from luminescence lifetimes and EXAFS measurements that the average coordination of Eu(III) in Na-Y is identical to that in aqueous solution because of the large aperture diameter (7.4 Å) of Na-Y. Thus, it appears that the Tb(III) ions in an unheated sample are fully hydrated as Eu(III) in Na-Y.

Spectral changes observed in fig. 1 can be characterized by the following two aspects. First, all the $^5D_4 \rightarrow {}^7F_j$ transition bands are inhomogeneously broadened with elevating the treatment temperatures. In particular, the $^5D_4 \rightarrow {}^7F_5$ transition band, which is observed at 547 nm in the emission spectrum of unheated TbNa-Y, begins to split into two bands at 544 and 551 nm from the temperatures higher than 373 K. Second, the $^5D_4 \rightarrow {}^7F_j$ transition bands show a remarkable increase in the band intensity when the treatment temperature is higher than 573 K. For example, the $^5D_4 \rightarrow ^7F_5$ transition band from the TbNa-Y treated at 773 K is approximately ten times stronger than that from unheated TbNa-Y. Apparently, thermal treatments of TbNa-Y at elevated temperatures result in the loss of water molecules from the first coordination shell of Tb(III) ions and thus the local symmetry of cations is lowered. If the Tb(III) ions are still placed in supercages without migrating to inner sites of the zeolite even after thermal treatments, the site symmetry of Tb(III) ions distorted by water loss could be restored to the original state by the subsequent rehydration. If such is the case, the emission spectra of TbNa-Y rehydrated after thermal treatments should be quite similar to that of unheated TbNa-Y. As seen in fig. 1, however, the TbNa-Y samples treated at temperatures higher than 373 K are not restored to the emission spectrum of unheated TbNa-Y by rehydration. Also, the emission spectra of these samples are not changed by re-exchange with Na(I), indicating that the Tb(III) ions are placed at non-exchangeable sites after thermal treatments. Therefore, it is most likely that the spectral changes caused by thermal treatments result from the irreversible migration of Tb(III) ions from supercages to inner sites in sodalite cages or hexagonal prisms.

Another important factor leading to changes in the emission spectra may be the coordination of the cation with zeolite framework oxygens. Hazenkamp et al. [10,11] demonstrate that unlike those in hydrated zeolite Y, the Gd(III) or Eu(III) ions in supercages of hydrated zeolite A are bound to framework oxygens because of steric constraints. Table 1 shows that the number of water molecules per unit cell for the TbNa-Y samples treated at elevated temperatures is smaller than that of unheated TbNa-Y. Thus, it appears that after the migration to inner sites of the zeolite, the Tb(III) ions are bound to framework oxygens as well as water molecules. This is not unexpected since the diameter of sodalite cages or hexagonal prisms is much smaller than that of supercages. As described earlier, the number of water molecules per unit cell is almost constant in the temperature region of 423–573 K and then decreases from temperatures higher than 573 K. Also, recall that the intensities of emission bands are not significantly changed in the temperature region of 300–573 K, but they are remarkably enhanced at temperatures higher than 573 K. These observations suggest that a decrease in the number of water molecules of the TbNa-Y samples from temperatures higher than 573 K may be related to an increase in the emission band intensity. Horrocks and Sudnick [15] show that the OH oscillators in water molecules quench the luminescence of Tb(III) ions by a nonradiative deexcitation pathway due to energy transfer to vibrational overtones of the OH moiety. Zeolite framework oxygens cannot function in this manner. Therefore, the enhancement of emission bands could be attributed to the coordination of Tb(III) ions with framework oxygens as well as the loss of water.

The exact location of the Tb(III) ions migrated to inner sites of the zeolite is difficult to ascertain. Fig. 2 displays the framework structure of zeolite Y. The different cation sites are represented by Roman numerals. The site nomenclature is given in table 2 together with the ideal site symmetry [6]. Table 2 shows that site I in hex-

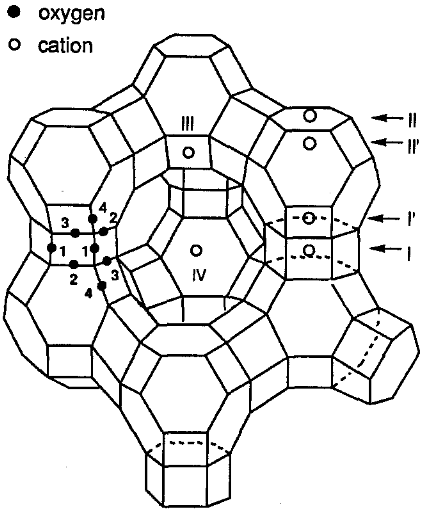

Fig. 2. Faujasite structure. The different cation positions are represented by Roman numerals. The four different types of framework oxygen atoms are indicated by the numbers 1–4.

agonal prisms has higher symmetry (O_h) than any other sites in sodalite cages or in supercages. Each set of sites except site IV in table 2 is of course not homogeneous in the actual zeolite crystal because of differences in the Si, Al ordering of crystallographically equivalent sites. Also, the participation of second-neighboring oxygens in the coordinative bonding must result in the distortion from the ideal site symmetry. However, such symmetry-lowering factors are of second-order importance so that they may lead to some broadening of the spectroscopic signals rather than essential changes [6]. Rare-earth ions are speculated to occupy site IV rather than sites II and III in supercages when exchanged into faujasite-type zeolites [14]. This appears to be reasonable since the cations cannot be fully hydrated at sites II and III. It is well known that the band intensity of electric-dipole $4f^n \rightarrow 4f^n$ transitions depends strongly on the site symmetry and the chemical bonding of the rare-earth ion [18,19], but magnetic-dipole transitions are not sensitive to variations in the local environment of the cation. Because of the odd parity of the elec-

Table 2
Cation site nomenclature and ideal site symmetry in faujasite structure

Site	Location	Ideal point symmetry
I	hexagonal prism	O_h
I'	sodalite cage	C_{3v}
II	supercage	C_{3v}
II'	sodalite cage	C_{3v}
III	supercage	C_{4v}
IV	supercage	–

tric-dipole operator, electric-dipole transitions are basically forbidden in an environment which has a center of inversion. Although the emission band intensity depends on various factors such as level of rare-earth loading or orientation of zeolite particulates, the band intensity ratio of electric-dipole to magnetic-dipole transition with respect to treatment temperature can provide some insight into the cation location. The $^5D_4 \rightarrow {}^7F_5$ transition band observed at 547 nm in the emission spectra of unheated TbNa-Y is assigned to the electric-dipole transition and the neighboring bands are magnetic-dipole transitions [19,20]. Fig. 3 shows plots of the band intensity ratio of $^5D_4 \rightarrow {}^7F_5$ to $^5D_4 \rightarrow {}^7F_6$ transition versus treatment temperature. Three different regions can be distinguished regardless of the excitation wavelength used. The band intensity ratio first increases from room temperature up to 473 K (region I) and then a significant decrease is observed between 473 and 523 K. Finally, the band intensity ratio remains almost unchanged from 523 to 773 K (region III). Thus, it is most likely that the site symmetry of the cations is gradually lowered in region I, but it becomes higher in region II. In addition, the consistency of the band intensity ratio in region III reveals that no further variations in the site symmetry are caused by thermal treatments in this temperature region. The rotational motions of the Tb(III) ions in supercages of hydrated Na-Y may be so fast enough to achieve random orientation since the cations are surrounded only by water molecules as those in aqueous solution. However, such rotational motions can be restricted to some extent by the coordination of cations with framework oxygens after the migration to inner sites of the zeolite. If this speculation is correct, differences in the actual site symmetry should be observed in a similar manner to those in the ideal site symmetry. This suggests that changes in the intensity ratio could be correlated with differences in the actual site symmetry,

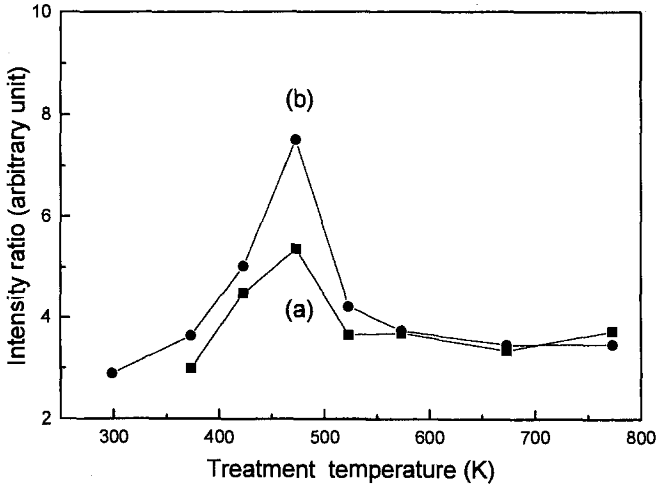

Fig. 3. Plots of intensity ratio of $^5D_4 \rightarrow {}^7F_5$ to $^5D_4 \rightarrow {}^7F_6$ transition band from TbNa-Y vs. treatment temperature. The excitation wavelength: 232 nm (a) and 378 nm (b).

although an unequivocal assignment to the symmetry of inner cation sites is not possible. Recall that site I in hexagonal prisms has the ideal site symmetry higher than that of site I′ or site II′ in sodalite cages. Therefore, it can be concluded from the intensity ratio changes illustrated in fig. 3 that most of the Tb(III) ions in supercages primarily migrate to site I′ or site II′ in sodalite cages below 473 K and then migrate to site I in hexagonal prisms at 473–523 K. There is some controversy concerning the preference for site I versus site I′. A significant decrease of the intensity ratio at 473–523 K clearly shows that the Tb(III) ions prefer site I to site I′ at higher treatment temperatures. This demonstrates that the migration of Tb(III) ions to specific sites is dependent on the treatment temperature. Further evidence to support the conclusion drawn from emission data will be given below.

3.3. EXCITATION SPECTRA

Fig. 4 shows the excitation spectra of TbNa-Y zeolites treated at different temperatures. Fig. 4a was obtained from unheated TbNa-Y, which consists of a very strong and broad band at 220 nm and numerous weak bands between 300 and 400 nm. These bands can be assigned to the $^7F \rightarrow {}^7D$ transition between 4f and 5d levels and the $^7F_j \rightarrow {}^5D_3$ transitions between 4f and 4f levels, respectively [21,22]. The band position for the $^7F \rightarrow {}^7D$ transition is in good agreement with that obtained from Tb(III) doped into YPO_4 crystals [21] or $Y_2O_3 \cdot P_2O_5$ glasses [23]. The excitation band intensities of $^7F_j \rightarrow {}^5D_3$ transitions between 4f and 4f levels are notably changed with elevating treatment temperature, but their band positions are not. The electric-dipole $^7F_6 \rightarrow {}^5D_3$ transition band at 378 nm is more enhanced

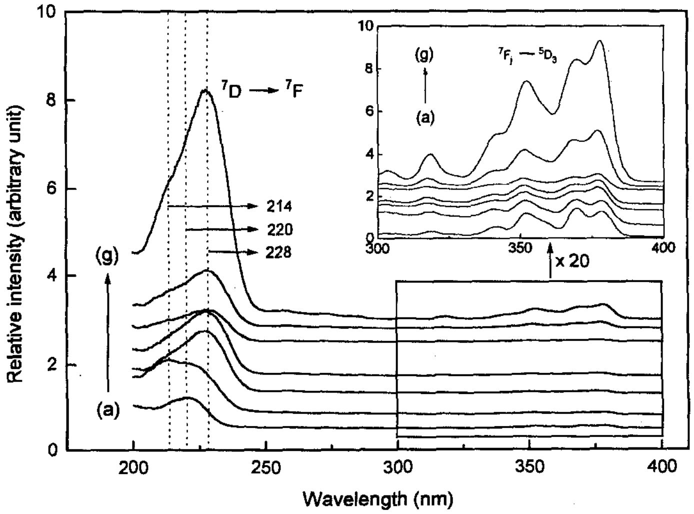

Fig. 4. Corrected excitation spectra of a series of TbNa-Y zeolites. The treatment temperatures are the same as those of fig. 1. The emission wavelength is 545 nm.

than the neighboring magnetic-dipole transition band by heating up to 773 K. This trend is consistent with that of the $^5D_4 \rightarrow {}^7F_6$ transition band observed in the emission spectra. An important observation obtained from fig. 4 is that with elevating the treatment temperature the $^7F \rightarrow {}^7D$ transition shows distinct changes in the relative density, position and number of bands. Fig. 4b was obtained after the TbNa-Y was treated at 373 K. In the spectrum, a new band at 214 nm as well as the band at 220 nm are observed. On the other hand, the band at 220 nm shifts to 228 nm when TbNa-Y was treated at temperatures higher than 423 K. Further shift of this band is not observed by heating up to 773 K. The band at 214 nm becomes weak by thermal treatment at temperatures higher than 423 K, but it does not disappear. This band is observed as a shoulder in parts c–g of fig. 4.

The band positions of $4f^n \rightarrow 4f^{n-1}5d$ transitions for rare-earth ions doped into inorganic glasses or crystals are reported to be very sensitive to variations in the site symmetry around cations [24,25]. For example, Brixner et al. [24] show that the $^7F \rightarrow {}^9D$ transition band of Tb(III) arising from a C_{3v} environment in LuOCl appears at 262 nm, while that of the cation in sites with C_{4v} symmetry of LaOCl is at 250 nm. Such changes may be due to the splitting of the five-fold 5d orbitals by the crystal field of the surrounding ligands as well as the energy gap between 4f ground state and the center of the gravity of 5d excited levels. We have recently found that the $^7F \rightarrow {}^7D$ transition band observed at 221 nm in the excitation spectrum of unheated TbNa-A shifts to 217 nm when the sample is heated at temperatures higher than 373 K [26]. Note that the ideal symmetry of sites in sodalite cages of zeolite A is identical to that of sites in sodalite cages of zeolite Y. Like the band at 220 nm, therefore, the two bands appearing at 214 and 228 nm in fig. 4b are also due to the $^7F \rightarrow {}^7D$ transition of the Tb(III) rather than the other transitions between 4f and 5d levels. However, they may originate from the cations at sites different from site IV. According to Krishnamurthy and Schaap [27], the relative energy of the lowest d orbital among the five-degenerated d orbitals by crystal field splitting in O_h, is much lower than that in C_{3v} because of the higher crystal field stabilization energy (CFSE). Thus, the most likely candidates for sites represented by bands at 214 and 228 nm may be site I′ or site II′ in sodalite cages, and site I in hexagonal prisms, respectively. The occurrence of the band at 214 nm before the shift of the band at 220 nm to 228 nm indicates that the Tb(III) ions first migrate to site I′ or site II′ in sodalite cages and in turn migrate to site I in hexagonal prisms. The preference of site I to site I′ appears to be reasonable because site I has a CFSE higher than site I′. Also, the presence of a shoulder at 214 nm in the spectra of TbNa-Y treated at temperatures higher than 423 K reveals that some portion of Tb(III) ions is still placed in sodalite cages even after thermal treatments up to 773 K. Therefore, it can be concluded that distinct dependence of the $^7F \rightarrow {}^7D$ transition for the Tb(III) ion on varying treatment temperature provides valuable information on the migration pathway as well as the intrazeolitic distribution of cations.

Previous luminescence studies involving rehydration of the dehydrated rare-earth-ion-exchanged zeolites show that well-resolved emission bands observed in the hydrated systems are not usually regenerated [14]. Our luminescence results are different from previously reported data in that not only the intensities of luminescence bands for Tb(III) ions are remarkably enhanced by elevating treatment temperature, but also their full-widths at half-maximum of the luminescence bands from the samples treated at elevated temperatures are still comparable to those from the unheated samples.

In conclusion, the overall results of this study suggest that distinct changes observed in the luminescence spectra of TbNa-Y zeolites rehydrated after thermal treatments at different temperatures can be correlated with differences in the site symmetry of the Tb(III) ion. This reveals that most of the Tb(III) ions in supercages of the zeolite irreversibly migrate to sodalite cages at temperatures lower than 473 K and then migrate to hexagonal prisms at the temperature region of 473–523 K. In addition, our luminescence data on TbNa-Y zeolites show that luminescence spectroscopy can be useful to study thermal effects on the intrazeolitic distribution of Tb(III) ions, in particular, to determine their migration temperatures to specific sites in zeolites.

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References

[1] S. Bhatia, in: *Zeolite Catalysis: Principles and Applications* (CRC, Boca Raton, 1990).
[2] J.M. Bennett and J.V. Smith, Mater. Res. Bull. 3 (1968) 865.
[3] M.L. Costenoble, W.J. Mortier and J.B. Uytterhoeven, J. Chem. Soc. Faraday Trans. I 74 (1978) 466.
[4] A.K. Cheetham, M.M. Eddy and J.M. Thomas, J. Chem. Soc. Chem. Commun. (1984) 1337.
[5] F. Roessner, K.H. Steinberg and H. Winkler, Zeolites 7 (1987) 47.
[6] R.A. Schoonheydt, Catal. Rev. Sci. Eng. 35 (1993) 129.
[7] K.-J. Chao and J.-Y. Chern, J. Phys. Chem. 93 (1989) 1401.
[8] L.B. Welsh and S.L. Lambert, ACS Symp. Ser. 368 (1988) 33.
[9] C.-F. Lin and K.-J. Chao, J. Phys. Chem. 95 (1991) 9411.
[10] M.F. Hazenkamp, A.M.H. van der Veen and G. Blasse, J. Chem. Soc. Faraday Trans. 88 (1992) 133.
[11] M.F. Hazenkamp, A.M.H. van der Veen, N. Feiken and G. Blasse, J. Chem. Soc. Faraday Trans. 88 (1992) 141.
[12] T. Arakawa, T. Takata, G.-Y. Adachi and J. Shiokawa, J. Chem. Soc. Chem. Commun. (1979) 453.

[13] T. Arakawa, T. Takata, M. Takakuwa, G.-Y. Adachi and J. Shiokawa, Mater. Res. Bull. 17 (1982) 171.

[14] J.F. Tanguay and S.L. Suib, Catal. Rev. Sci. Eng. 29 (1987) 1.

[15] W.D. Horrocks Jr. and D.R. Sudnick, J. Am. Chem. Soc. 101 (1979) 334.

[16] A. Habenschuss and F.H. Spedding, J. Chem. Phys. 70 (1979) 2797.

[17] S.L. Suib, R.P. Zerger, G.D. Stucky, T.I. Morrison and G.K. Shenoy, J. Chem. Phys. 80 (1984) 2203.

[18] Y. Haas and G. Stein, J. Phys. Chem. 75 (1971) 3668.

[19] F. Bergaya and H. van Damme, J. Chem. Soc. Faraday Trans. II 79 (1983) 505.

[20] O.J. Sovers, M. Ogawa and T. Yoshioka, J. Luminescence 18/19 (1979) 336.

[21] T. Takahashi and O. Yamada, J. Electrochem. Soc. 126 (1979) 2206.

[22] R. Chen, J. Huang, L. Lu and Y. Xu, Mater. Res. Bull. 23 (1988) 1699.

[23] T. Hoshina and S. Kuboniwa, J. Phys. Soc. Jpn. 31 (1971) 838.

[24] L.H. Brixner, J.F. Ackerman and C.M. Foris, J. Luminescence 26 (1981) 1.

[25] C. Dujardin, B. Moine and C. Pedrini, J. Luminescence 54 (1993) 259.

[26] S.B. Hong, E.W. Shin, S.H. Moon, C.-H. Pyun, C.-H. Kim and Y.S. Uh, submitted.

[27] R. Krishnamurthy and W.B. Schaap, J. Chem. Educ. 46 (1969) 799.