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Encapsulation of nitrophenol into AlPO$_4$-5: Effect of isomers on optical second harmonic generations

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Three isomers of nitrophenol molecules were loaded in one-dimensional channels of AlPO$_4$-5 by vapor-phase diffusion process. The resulting materials (*o*-NP/, *m*-NP/ and *p*-NP/AlPO$_4$-5) have been characterized by thermoanalytic and spectroscopic methods, and their nonlinear optical properties have been investigated in powder form. From the results, these materials were found to exhibit second harmonic generation (SHG). The order of SHG intensity was *m*-NP/AlPO$_4$-5 $<$ *p*-NP/AlPO$_4$-5 $<$ *o*-NP/AlPO$_4$-5, and SHG intensity of *o*-NP/AlPO$_4$-5 remarkably depended on amount of loadings. © *1999 Kluwer Academic Publishers*

1. Introduction

The inorganic and organic clusters, synthesized in the lattice space of zeolites and layer compounds as reaction vessels, have been expected to bring about the unusual physical properties. For example, potassium clusters prepared in the cages of zeolite LTA exhibit ferromagnetic properties [1, 2]. And *p*-nitroaniline (*p*-NA) and 2-methyl-*p*-nitroaniline clusters encapsulated in noncentrosymmetric molecular sieves, AlPO$_4$-5, VPI-5, and ZSM-5, bring about nonlinear optical properties, i.e., second harmonic generation (SHG) [3–7]. The geometrical arrangement of *p*-NA clusters in channels of AlPO$_4$-5 was investigated by Raman, polarized IR, and UV-Vis spectroscopy [8–11]. The effects of the isomers encapsulated in zeolitic channels on the nonlinear optical properties have not, however, been reported yet.

In this paper, we report the encapsulation of three isomers of nitrophenol (*o*-NP, *m*-NP and *p*-NP) molecules in the one-dimensional 12-ring channels of AlPO$_4$-5 and the nonlinear optical properties of the resulting materials (*o*-NP/, *m*-NP/ and *p*-NP/AlPO$_4$-5). The detectable nonlinear optical property was expected to be derived by self-oriented aggregate of nitrophenol molecules in the channels with the free diameter value of 7.3 Å, which is enough size to occlude nitrophenol molecules [12], although a dipole moment of nitrophenol molecule is smaller than that of nitroaniline molecule. Moreover configuration of donor-acceptor-substituents, —OH and —NO$_2$, might affect the nonlinearity, because the charge transfer by the configuration inflences the distortion of π electrons of benzene ring.

2. Experimental

AlPO$_4$-5 was hydrothermally prepared, using starting materials such as boemite (Shokubai Kasei) and phosphoric acid (85% Wako), and a template such as tri-*n*-propylamine (Pr$_3$N, Tokyo Kasei). Phosphoric acid was added to boemite dispersed in deionized water with continuous stirring. Finally Pr$_3$N was added, and the mixture was stirred further for 1 h to obtain a homogeneous mixed gel. The mixed gel, $Al_2O_3 : P_2O_5 : Pr_3N : 150H_2O$, was loaded in a teflon-lined autoclave, and heated at 170 °C for 48 h. The products were decanted, washed repeatedly with deionized water, and finally dried at 60 °C.

After calcination at 750 °C to eliminate templates, AlPO$_4$-5 hosts and nitrophenol guests were weighted into respective ampoules, which were connected to a vacuum line. Zeolitic water was eliminated at 200 °C under 0.02 Pa for 5 h. After evacuated treatment, the organic guests were loaded by vapor-phase diffusion process for 12 h at 90 °C for *o*-NP, at 120 °C for *m*-NP

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and *p*-NP, respectively, considering respective melting point under atmospheric pressure. The loadings into the host were controlled by the amounts of sublimed guests.

The resulting materials were examined by powder X-ray diffraction (XRD) with monochromated CuK_α radiation, using a Rigaku RAD-IIC diffractometer, and thermal analysis (TG-DTA) at heating rate of 10 °C·min^{-1} up to 1000 °C, using a Rigaku TAS-100 instrument. Spectroscopic characterizations were made in two ways; (a) Fourier transform infrared (FTIR) spectra by KBr methods in the range 4000–400 cm^{-1}, using a JASCO FT/IR 350 spectrometer, and (b) diffuse-reflectance ultraviolet-visible (UV-Vis) spectra in the range 250–800 nm, using a Shimazu UV-2100PC spectrometer. SHG intensities relative to an urea reference were measured by the powder technique [13], using a Q-switched Nd: YAG laser ($\lambda = 1064$ nm).

3. Results and discussion

TG-DTA curves of NP/$AlPO_4$-5 are shown in Fig. 1. The weight losses below 150 °C and endothermic peaks below 100 °C on TG-DTA curves of the specimens were assigned to the desorption of water molecules. The weight losses in the range 150–500 °C were assigned to the combustion of occluded nitrophenol molecules, showing the exothermic peaks at about 300 °C. Endothermic peaks were observed in the range from 200–300 °C on the DTA curves of specimens with loadings greater than 12, 4, and 9 mass % for *o*-, *m*-, and *p*-NP, respectively. These endothermic peaks were considered to be due to the desorption of excess nitrophenol molecules, which were adsorbed on the surface of $AlPO_4$-5 crystals. The maximum amounts of *o*-, *m*-, and *p*-NP encapsulated in the one-dimensional channels of $AlPO_4$-5 were, therefore, estimated to be about 12, 4, and 9 mass %, respectively. The amounts of nitrophenol molecules were a little small, compared with a maximum amount of *p*-NA, i.e., 13 mass % [3–5]. The amount of loading was supposed to be governed by the difference of steric array of guest molecules in the channels.

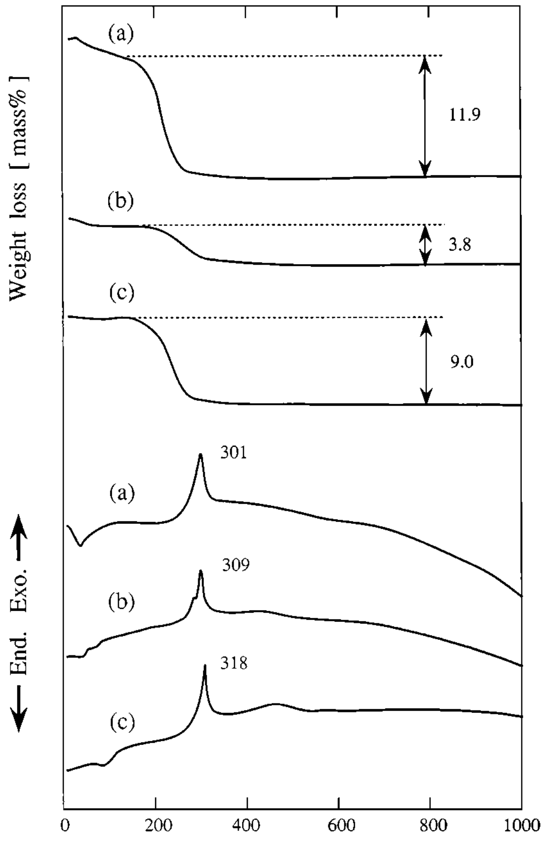

Figure 1 TG-DTA curves of: (a) *o*-NP/$AlPO_4$-5; (b) *m*-NP/$AlPO_4$-5 and; (c) *p*-NP/$AlPO_4$-5.

The XRD patterns of specimens before and after encapsulation of nitrophenol molecules are shown in Fig. 2. Host materials, which have good crystallinity without impurity, were identified as $AlPO_4$-5. XRD revealed that each NP/$AlPO_4$-5 maintained the $AlPO_4$-5 structure, and there were no peaks caused by nitrophenol guests. The peak intensity at $2\theta = 7.4°$ was remarkably weakened and those at $2\theta = 21.0, 22.4, 25.9, 30.0°$, and so on were strengthened by loadings of *o*- and *p*-NP, whereas the noticeable change of the peak intensities was not observed by loading of *m*-NP.

FTIR spectra of specimens before and after encapsulation of nitrophenol molecules and nitrophenol guests are shown in Fig. 3. Each spectrum of NP/$AlPO_4$-5 showed characteristic absorption peaks of respective guest molecules in the range below 2000 cm^{-1}, though certain shifts of IR peaks were observed. The results of XRD and FTIR suggested that nitrophenol molecules were incorporated in the lattice space of $AlPO_4$-5. The absorption bands based on hydrogen bonds within a molecule or between molecules could not, however, be

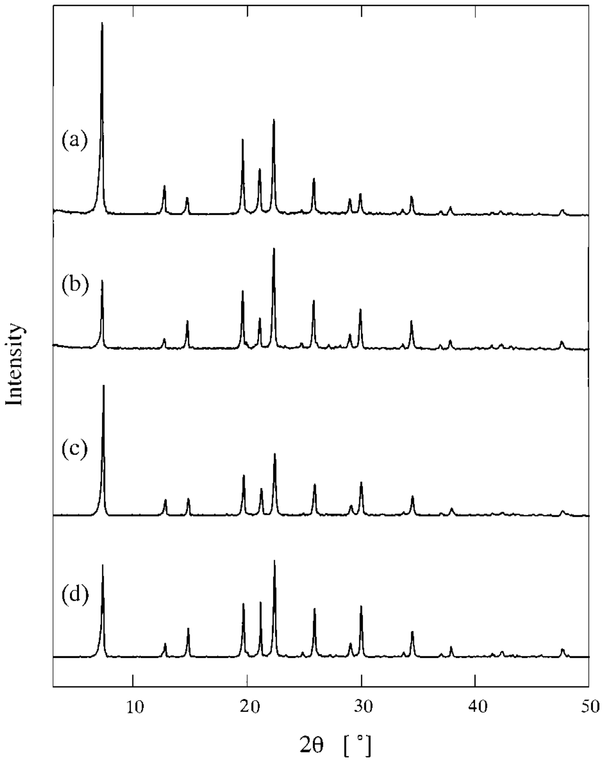

Figure 2 XRD patterns of: (a) $AlPO_4$-5; (b) 11.9 mass % *o*-NP/$AlPO_4$-5; (c) 3.8 mass % *m*-NP/$AlPO_4$-5 and; (d) 9.0 mass % *p*-NP/$AlPO_4$-5.

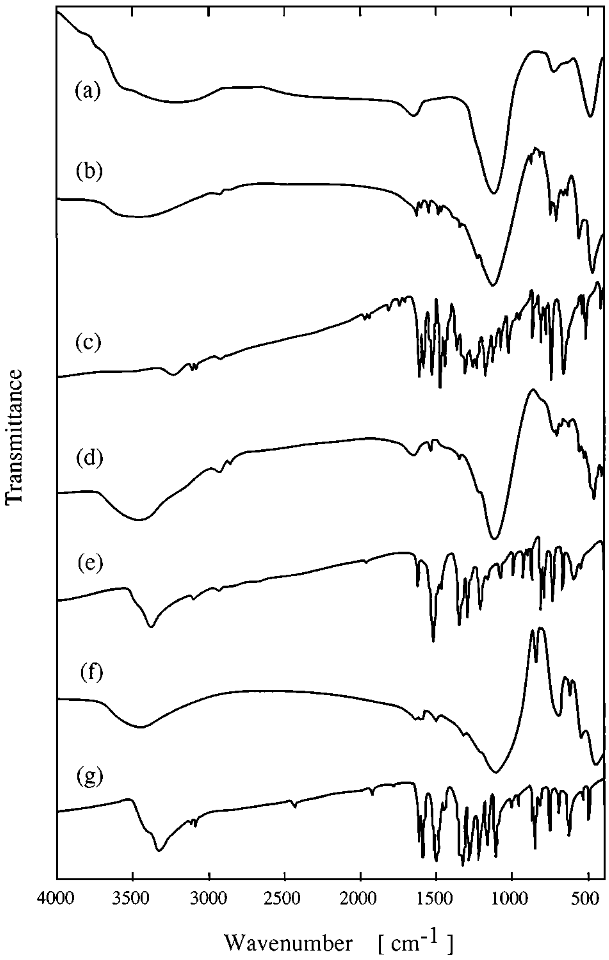

Figure 3 FTIR spectra of: (a) $AlPO_4$-5; (b) 11.9 mass % *o*-NP/$AlPO_4$-5; (c) *o*-NP molecules; (d) 3.8 mass % *m*-NP/$AlPO_4$-5; (e) *m*-NP molecules; (f) 9.0 mass % *p*-NP/$AlPO_4$-5 and; (g) *p*-NP molecules.

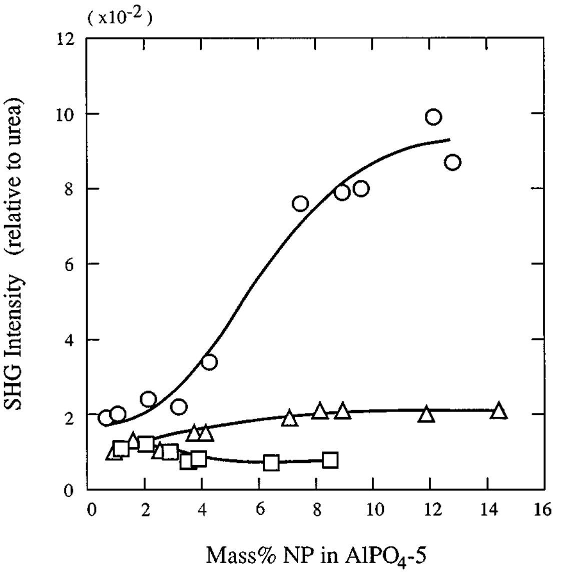

Figure 4 SHG intensities of *o*-NP/$AlPO_4$-5 (○), *m*-NP/$AlPO_4$-5 (□) and *p*-NP/$AlPO_4$-5 (△) as a function of loadings in $AlPO_4$-5.

distinctly observed in the vicinity of 3200 cm^{-1}, indicating the interaction between molecules was weak.

The SHG intensities of NP/$AlPO_4$-5 as a function of loadings in $AlPO_4$-5 are shown in Fig. 4. The SHG signals of *o*-NP/, *m*-NP/ and *p*-NP/$AlPO_4$-5 were observed, suggesting these materials had nonlinear optical properties, although their intensities were weak compared with *p*-NA/$AlPO_4$-5 [3–5], whose SHG intensity was about seven times as strong as that of *o*-NP/$AlPO_4$-5. The differences of the SHG intensities among these materials were noticeable. Namely, contrary to our expectations, the SHG intensity of *o*-NP/$AlPO_4$-5 was stronger than that of *p*-NP/$AlPO_4$-5, and was about 4.5 times at 12 mass % loading. The SHG intensity of *o*-NP/$AlPO_4$-5 strongly depended on amount of loadings, and was saturated at about 12 mass % loading, while that of *p*-NP/$AlPO_4$-5 weakly depended on amount of loadings, and was saturated at about 10 mass % loading. The SHG intensity of *m*-NP/$AlPO_4$-5 was weakest, and the dependence of the SHG on loading was scarcely observed. This was considered to be due to the fact that it was difficult to encapsulate *m*-NP molecules greater than 4 mass % loading, and further the arrangement of *m*-NP molecules in the channels went out of order.

The theoretical hyperpolarizabilities, β, on *o*-, *m*- and *p*-NP were speculated in order to explain the order of the experimental SHG intensities, i.e., *m*-NP/$AlPO_4$-5 < *p*-NP/$AlPO_4$-5 < *o*-NP/$AlPO_4$-5. The second-order polarizability tensor, d, is proportional to β[14], and the SHG intensity by powder technique, SHG_{powder}, is proportional to square of d_{eff} [13].

$$d \propto \beta$$

$$SHG_{powder} \propto d_{eff}^2$$

Here, d_{eff} is an averaged value for d. Thus, SHG_{powder} is proportional to square of β.

$$SHG_{powder} \propto \beta^2$$

The βs were calculated using MOPAC [15], provided that the direction of the x axis of molecule is along the one-dimensional channel and those of the y and z axes are random. Their wavelength dispersions were calculated, using the two level model [16] with the transfer energies obtained from UV-Vis absorption spectra of NP/$AlPO_4$-5. The values of β along the dipole moment were estimated to be 0.2×10^{-30}, 0.9×10^{-30} and 3.0×10^{-30} esu for *o*-, *m*- and *p*-NP, respectively. However, as the experimental results were extremely different from the estimation, they were considered to be ascribed to the factors other than the resonance effect. The variation of β by the interaction between substituents and host lattice must be trivial, because the significant difference between UV-Vis absorption spectra of bulk nitrophenol and NP/$AlPO_4$-5 was hardly observed. The SHG intensity of *o*-NP/$AlPO_4$-5 was, therefore, guessed to be enhanced by the geometrical arrangement of *o*-NP molecules with high orientation in the channels and/or by the phase matching. The geometrical arrangements of nitrophenol molecules in the channels were supposed as schematically shown in Fig. 5, provided that the values of the βs were directly reflected in the experimental values of the SHG intensities. Namely, the direction of β on *o*-NP/$AlPO_4$-5 is nearly along the *c* axis of the host, whereas that on *p*-NP/$AlPO_4$-5

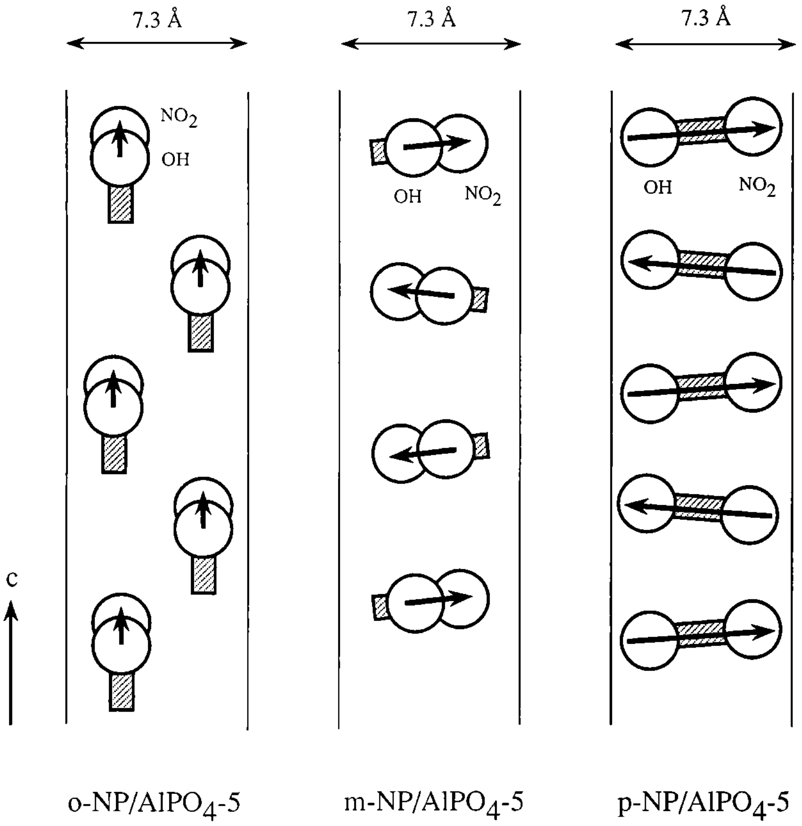

Figure 5 Schematic illustrations of geometrical arrangements of nitrophenol molecules in the one-dimensional channels of $AlPO_4$-5 predicted from observed SHGs and calculated βs. Rectangle with diagonal lines and arrow represent benzene ring and vector β, respectively.

probably quite leans to the direction perpendicular to the c axis. Consequently, the component of β along the c axis on p-NP/$AlPO_4$-5 becomes smaller than that on o-NP/$AlPO_4$-5. Molecules may not come close each other, because hydrogen bonds were not observed. m-NP molecules are more loosely loaded, and although the direction of β also leans to the direction perpendicular to the c axis, some molecules probably face in the opposite direction. In any case, the geometrical arrangements of nitrophenol molecules in the channels based on the structural analysis could be discussed in a following paper.

In conclusion, three isomers of nitrophenol molecules were encapsulated in the one-dimensional channels of $AlPO_4$-5 by vapor-phase diffusion process, and the maximum amounts of loadings for o-, m-, and p-NP were estimated to be about 12, 4, and 9 mass %, respectively. The resulting materials were found to exhibit nonlinear optical properties. It is noticeable that the order of the SHG intensities was m-NP/$AlPO_4$-5 < p-NP/$AlPO_4$-5 < o-NP/$AlPO_4$-5, and the SHG intensity of o-NP/$AlPO_4$-5 drastically increased with increasing loadings up to about 12 mass % loading.

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