

Second-Order Nonlinearity of Mixtures Including *p*-Nitroaniline Derivatives

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We have demonstrated the evaluation of nonlinear optical properties and the determination of the molecular orientation of the mixed crystals of *p*-nitroaniline (*p*-NA) and *N*-ethyl-4-nitroaniline (NENA) in powder form. Although neither material shows second-order nonlinearity due to the crystalline structure, the obtained mixture shows high optical nonlinearity because it includes the mixed crystals, which are noncentrosymmetric. We measured the second-order nonlinear optical efficiency of the mixture using the second-harmonics with evanescent wave (SHEW) technique. The SHEW technique can be applied to the compound in powder form, so that not only the nonlinear optical property of a mixture, which consists of several materials, but also that of mixed crystals, which are difficult to make in a certain size of single crystal for the usual measurement such as the Maker fringe measurement, are able to be characterized. The efficiency of the mixture corresponded well with the area of the X-ray diffraction peak that appeared after mixing, i.e., the amount of the new mixed crystal. This indicates that the SHEW technique can be used as a monitor of the crystalline structure. With the results of the X-ray powder diffraction, the angular averaged second-order nonlinear coefficient of the newly formed mixed crystal was obtained to be 86 ± 15 pm/V. This result suggests that molecules are aligned almost parallel in the mixed crystal.

Introduction

Many organic materials for second-harmonic generation (SHG) have been developed because of the variety of the synthesis. The molecules with donor–acceptor conjugated systems have large hyperpolarizabilities because of the large charge transfer inside the molecules. Although such molecules show high microscopic nonlinearity, when they form a crystal, the macroscopic nonlinearity often disappears because of the centrosymmetry of the crystal. The dipole moment of these molecules is so large that they tend to have centrosymmetric packing to cancel out their dipoles, and this is often a serious problem.

One of the well-known molecules with a large hyperpolarizability is *p*-nitroaniline (*p*-NA). Due to the high polarizability induced by the donor–acceptor pair, *p*-NA molecules in crystals align to cancel out the polarization. The crystal is thus centrosymmetric and shows no SH activity. There have been many attempts to utilize the high molecular nonlinearity of *p*-NA, such as blending it with polymers,¹ loading it in molecular-sieve hosts,^{2,3} and attempting to change the crystalline structure by making mixed crystals with similar materials.⁴ These studies, particularly controlling the crystalline structure, are very interesting from the point of view not only of making highly effective nonlinear materials but also of the crystal engineering. The SHG efficiency of materials is deeply related to the crystalline structure; thus it can be one of the indicators of the structure.

Although the crystalline structure can be controlled, it is difficult to grow a single crystal for the evaluation of SHG efficiency. Thus, the conventional powder technique⁵ has been applied to evaluate the nonlinearity of these materials. However, the result of the powder technique depends not only on the efficiency of the material but also on the powder size and the birefringent phase matchability. Therefore it shows only

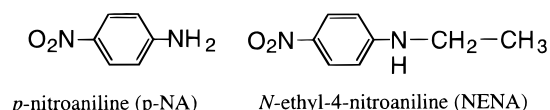


Figure 1. Structures of *p*-NA and NENA.

whether the material is SH active or not, that is, whether the crystal is noncentrosymmetric or not, much less the nonlinear optical coefficient d , nor detailed information about the crystalline structure.

On the other hand, we have demonstrated the SHEW (second-harmonic generation with evanescent wave) technique,⁶ which does not require a single crystal as a sample. Using the evanescent wave as a fundamental wave, this technique can provide results that do not depend on the phase matchability of the sample because the SHG of the transmission mode is suppressed and the reflection mode that is always phase-matched is observed. Additionally, even though the evanescent wave of the total reflection is used, the SHEW power is much larger than the surface SHG power, and the results reflect the property of the bulk crystal. Thus it is expected that the nonlinear optical property of the powder sample can be discussed quantitatively using the SHEW results.

We made a mixed crystal from *p*-NA and *N*-ethyl-4-nitroaniline (NENA), both of which have large hyperpolarizabilities, but form crystals with no second-order optical nonlinearity. We evaluated the second-order optical nonlinearity of the mixed crystal in powder form using the SHEW technique.

Experimental Section

We prepared mixtures of *p*-NA and NENA in various proportions by melting.⁴ The structures of these materials are shown in Figure 1. First, the materials were purified by column chromatography on silica gel using MeOH eluent for *p*-NA and benzene eluent for NENA and then recrystallized. This procedure was repeated until the SH wave from the pure materials could not be observed under the strong incident light. Then the purified materials were weighed and blended in a small

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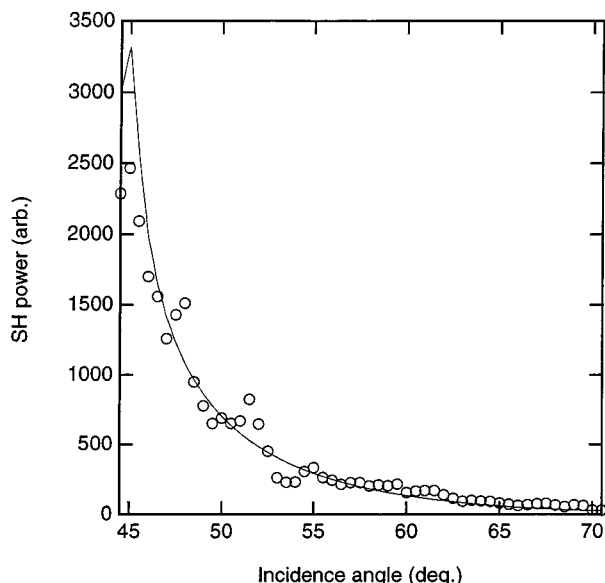


Figure 2. SHEW signals from the mixture. The circles represent the experimental data, and the solid line represents the fitted curve.

glass bottle, which was then dipped in an oil bath to melt the materials. The melting points of *p*-NA and NENA are 149 and 96–98 °C, respectively. The mixture was heated to 150 °C and cooled at about 20 °C/s. Since the SH activity of the mixed crystal decreases at room temperature because of the heat effect, we kept the samples under –80 °C.

The experimental setup of the SHEW technique is described elsewhere.⁶ The principle of the technique involves measuring the power of the SH wave in the reflection mode excited by the evanescent wave. The fundamental wave of a Q-switched Nd:YAG ($\lambda = 1064$ nm) was used as the incident wave. The SHEW signal from the mixture of 40 mol % NENA is shown in Figure 2. The SH power is measured by varying the incidence angle. The second-order nonlinear susceptibility is provided by the fitting and compared with the result of *m*-nitroaniline powders measured under the same conditions as a reference.

Result and Discussion

The crystalline structure of *p*-NA is centrosymmetric,⁷ and NENA has not been characterized, but neither shows any SH activity in pure crystals; nevertheless, the mixed crystals formed from them exhibited large second-order optical nonlinearity. The fact that neither material is SH active makes the SHEW results clear because the obtained value will be proportional to the amount of the new SH active crystal in the mixture.

We measured the X-ray powder diffraction of these mixtures to check the existence of the new crystal. The X-ray powder diffraction spectra for the mixtures at various material proportions are shown in Figure 3. The spectra are calibrated by the peak area of the NaCl blended in the sample. We observed two series of peaks corresponding to *p*-NA and NENA, as well as a new series of peaks, which do not appear in the spectra for pure materials. This means that a new crystal was formed by the mixing.

The same samples were examined using the SHEW technique to evaluate the nonlinear optical properties at various material proportions. Actually, the SHEW technique does not give each element of the *d* tensor, but gives an angular averaged value of each *d* element, and does it as well as the powder technique does.⁵ This is because the incident wave shines fine powder crystals in various directions, which excites all the tensor

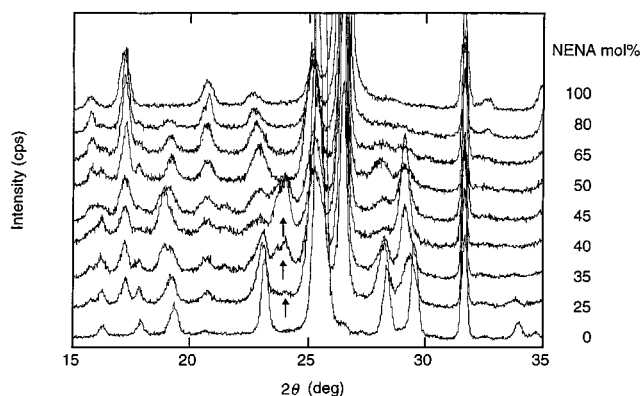


Figure 3. X-ray powder diffraction spectra of the mixture at various mixing ratios. The arrows indicate the new peaks for the mixed crystal.

elements and induces SH waves in various directions. The SHEW power also depends on the refractive indices of the sample, which vary according to the crystal direction in the case of a birefringent crystal. However, the effect from the differences of the refractive indices is so small that we use isotropic refractive indices for simplicity.

We measured the s-polarized SHEW power with the s-polarized incident light. Thus the measured *d* tensor is d_{FFF} , which is related to *d* in the molecular axis as⁸

$$d_{FFF} = \sum_{ijk} \Phi_{Fi} \Phi_{Fj} \Phi_{Fk} d_{ijk} \quad (1)$$

where Φ is the directional cosine between the laboratory-fixed *F* axis and the molecule-fixed *i* axis. The observed SHEW power is the summation of the SHEW powers from all the powder crystals that are incoherent. Thus, the obtained *d* value is described as

$$\langle d_{FFF}^2 \rangle = \langle (\sum_{ijk} \Phi_{Fi} \Phi_{Fj} \Phi_{Fk} d_{ijk})^2 \rangle \quad (2)$$

Using Kleinman's rule and considering $d_{ijk} = d_{ikj}$, this can be written as

$$\langle d_{FFF}^2 \rangle = \frac{1}{7} \sum_i d_{iii}^2 + \frac{6}{35} \sum_{i \neq j} d_{iii} d_{ijj} + \frac{9}{35} \sum_{i \neq j} d_{ijj}^2 + \frac{6}{35} \sum_{ijk, \text{cyclic}} d_{ijj} d_{jkk} + \frac{12}{35} d_{ijk}^2 \quad (3)$$

The actual value of $\sqrt{\langle d^2 \rangle}$ of the sample is derived by comparing it with the reference material. We use here *m*-nitroaniline (*m*-NA) as the reference because all the *d* tensor components are known. The *d* value of *m*-NA is

$$\langle (d_{(m-NA)})^2 \rangle = \frac{1}{7} d_{333}^2 + \frac{9}{35} (d_{311}^2 + d_{322}^2) + \frac{6}{35} (d_{311} d_{333} + d_{322} d_{333}) \quad (4)$$

Since the *d* values for *m*-NA are $d_{311} = 14 \pm 2$ pm/V, $d_{322} = 1.2 \pm 0.3$ pm/V, $d_{333} = 15 \pm 1$ pm/V, which are calculated from the literature value⁹ using the value for quartz $d_{111}(Q) = 0.364 \pm 0.04$ pm/V,¹⁰ $\sqrt{\langle (d_{(m-NA)})^2 \rangle}$ was calculated to be 11 ± 1 pm/V.

We compared the obtained *d* values with the results of X-ray diffraction. We measured the area of the new peaks at $2\theta = 24^\circ$ in the X-ray diffraction spectrum, which is proportional to the amount of the newly formed mixed crystal. On the other hand, the square of the *d* value is proportional to the amount of

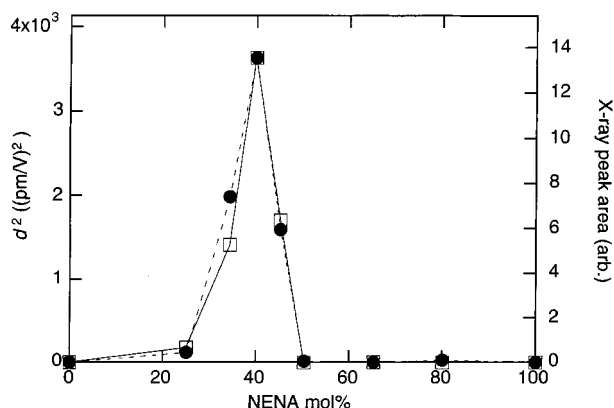


Figure 4. Comparison between the square of nonlinear coefficients and X-ray diffraction peak areas of the mixtures. The solid circles represent d^2 , and the open squares represent the X-ray diffraction peak area.

the new SH active crystal. As shown in Figure 4, it is found that the NENA ratio dependence of the area coincides with that of $d_{(\text{mix})}^2$ evaluated using the SHEW technique. The fact that the SHEW results reflect well the X-ray peak areas means that the new peaks observed in X-ray diffraction originate in the new SH active crystals. This also indicates that the SHEW technique can be a monitor of the crystal structural change if it is from a SH inactive crystal to a SH active crystal because the SH activity is sensitive to the crystalline structure.

We use here the effective value of the d coefficient as $d_{(\text{mix})}$ because the obtained sample was a mixture of the newly formed mixed crystal and the residual materials. The $d_{(\text{mix})}$ value for the mixture, which changed according to the mixing ratio, was maximized around 40 mol % NENA as $d_{(\text{mix})} = 60 \pm 8$ pm/V.

We must know the amount of the SH active mixed crystal included in the mixture at 40 mol % NENA to obtain the d value of this mixed crystal. The amount of the mixed crystal was estimated from the reduced amounts of the diffraction peak areas of p -NA and NENA because the cross section of X-ray diffraction for the new peak is not known. The peaks at 19° and 25° for p -NA, at 17° , 21° , 26° , and 35° for NENA were averaged to estimate the reduced amounts. Assuming that the entire quantity of molecules decreased from p -NA and NENA becomes the new mixed crystal, it accounts for 49 mol % of the mixture. Then the d value was corrected by the concentration of mixed crystal in the mixture, and the result was 86 ± 15 pm/V. Thus the sample, which is blended with SH inactive materials and cannot be separated like the mixture shown here, can be evaluated using the SHEW technique and powder X-ray diffraction.

There has been no technique that can provide information about the molecular orientation of such powder samples, much less for unseparable samples. We roughly estimate the molecular orientation using the d value for the new mixed crystal. We compare this value with 2-methyl-4-nitroaniline (MNA) because the d values of NENA and p -NA are zero. On the other hand, the hyperpolarizability of MNA is considered to be similar to those of NENA and p -NA,¹¹ and its d tensor and crystalline structure are already measured.

Using the quartz value $d_{111}(\text{Q}) = 0.364 \pm 0.04$ pm/V,¹⁰ d_{111} for MNA is 182 ± 46 pm/V and the tilt angle between two molecules $2\psi = 42^\circ$.¹² The value d_0 , which is the maximum value of d_{111} if $\psi = 0$, is calculated to be 224 ± 56 pm/V. It is reasonable to introduce d_0 because both NENA and p -NA are molecules with one-dimensional nonlinear dipoles. We calculate the tilt angle ψ for the mixed crystal from the SHEW result on the analogy of MNA. Assuming that the density of the mixed

crystal is equal to that of MNA, the d value for the new crystal obtained using the SHEW technique can be described as follows when the axes of coordinates are set appropriately to the molecular direction.

$$\begin{aligned} \langle (d_{(\text{New})})^2 \rangle &= \frac{1}{7}d_{111}^2 + \frac{9}{35}d_{122}^2 + \frac{6}{35}d_{111}d_{122} \\ &= d_0^2 \left(\frac{1}{7}\cos^6\psi + \frac{9}{35}\cos^2\psi\sin^4\psi + \right. \\ &\quad \left. \frac{6}{35}\cos^4\psi\sin^2\psi \right) \quad (5) \end{aligned}$$

Using the value $\langle (d_{(\text{New})})^2 \rangle = (86)^2$ and $d_0 = 224$, $\cos^2\psi$ was calculated to be 1.01, which means that the molecules are aligned almost parallel. Thus, the newly formed mixed crystal has a structure that makes the best use of the hyperpolarizability, and $d_{111}(\text{New}) \approx 1.2 d_{111}(\text{MNA})$. We assumed above that the vanished p -NA and NENA molecules create one phase of SH active crystal. If some of the molecules do not become part of the SH active crystal, the d value of the new crystal becomes larger, which results in the larger value of $\cos^2\psi$. This leads to being an ψ imaginary number. Therefore, the assumption that the mixture consists of three materials, p -NA, NENA, and a newly formed mixed crystal, is appropriate. The result estimated above is affected by the differences in density and hyperpolarizability between MNA and the mixed crystal, which must be small. However, more accurate information can be obtained by comparing the experimental result by the technique demonstrated here and the theoretical model for the crystalline structure, in which every value assumed above can be calculated.

Finally we try to explain the formation of the new crystal. The molecules that have a large dipole moment in the ground state tend to pack antiparallel to cancel it out, which is the stable state. This occurs frequently in the crystallization of the materials for nonlinear optics with a donor–acceptor system. In case of the mixture of p -NA and NENA, the SH activity decreased at room temperature. This means that the newly formed crystal, which is SH active, is considered to be an unstable state. The rapid cooling at 20°C/s realized the unstable state where the molecules are aligned parallel, such as shown here. The bulky substituent of NENA is considered to be a hindrance to avoid the molecules being antiparallel. This cannot occur until the concentration of NENA in the mixture reaches a certain value, on the other hand, a high concentration of NENA leads the character of NENA to be predominantly bulk crystal.

Conclusion

We evaluated the nonlinear optical property of the mixed crystal of p -NA and NENA. The existence of the new mixed crystal in the mixture was confirmed by X-ray powder diffraction, and the SHEW result corresponded well to the X-ray result. From these two results, we estimated the angular average of the d value of the mixed crystals to be 86 pm/V, which is larger than MNA. Using MNA as an analogy, the molecules in the mixed crystal of p -NA and NENA were roughly estimated to be aligned almost parallel. The SHEW technique is a powerful tool for evaluating nonlinear optical properties of unseparable samples and is potentially useful for estimating the crystalline structure. Using this technique, one can obtain information about the molecular alignment more easily. As it does not require single crystal, more materials can be examined systematically, which contributes to crystal engineering.

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