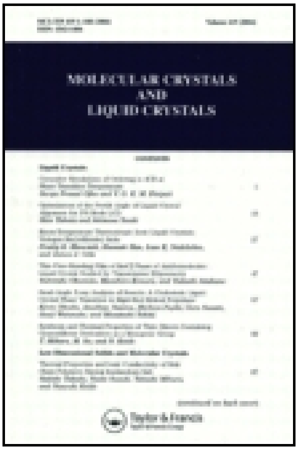

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF 2,7-DINITRO-9-FLUORENONE SINGLE CRYSTAL

Satoru Nakao [a], Hisayoshi Shiozaki [a], Yoshiaki Sakurai [a], Ayako Hioki [a], Masaki Kimoto [a], Fumito Araoka [b] & Hideo Takezoe [b]

[a] Materials Technology Department, Technology Research Institute of Osaka Prefecture

[b] Department of Organic and Polymeric Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF 2,7-DINITRO-9-FLUORENONE SINGLE CRYSTAL

Satoru Nakao, Hisayoshi Shiozaki, Yoshiaki Sakurai,*
Ayako Hioki, and Masaki Kimoto
Materials Technology Department,
Technology Research Institute of Osaka Prefecture

Fumito Araoka and Hideo Takezoe
Department of Organic and Polymeric Chemistry,
Graduate School of Science and Engineering,
Tokyo Institute of Technology

The linear and nonlinear optical properties of 2,7-dinitro-9-fluorenone single crystals are investigated, especially those affecting the usage for optical second-harmonic generation. Sufficient optical quality plate-like crystals have been grown by sublimation in purified nitrogen flow. The crystal is transparent in the visible and near-infrared region, is negative biaxial with $n_a > n_c > n_b$ *and has birefringence with* $n_a - n_b = 0.52$ *at 532 nm. The nonlinear optical coefficients determined by Maker fringe method are* $d_{33} = 8\,pm/V$ *and* $d_{32} = d_{24} = 0.4\,pm/V$*. Type I and type II critical phase matching are possible in the near infrared region and type I is preferable.*

Keywords: 2,7-dinitro-9-fluorenone; optical properties; phase matching; second harmonic generation

1. INTRODUCTION

In conjugated materials, the optical and electronic properties hinges on the properties of the delocalized π-electron system that permits charge transport within an individual molecule and between adjacent molecules. Both the structure of an individual molecule and the packing of the

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*Address correspondence to Satoru Nakao, Materials Technology Dept., Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan.

molecules play important part in characterization of these materials. For example, in nonlinear optical materials for second-harmonic generation (SHG) devices, spontaneous polarizable molecules with a π-conjugated skeleton, donor/acceptor substitution at the end of a π-conjugation and the noncentrosymmetric structure, e.g. 2-methyl-4-nitroaniline, are of interest because of their potential to have large second-order nonlinearities and a high-speed response [1,2].

2,7-Dinitro-9-fluorenone (DNF) is one of the polynitro-substituted fluorenones (NFs). The NFs are well-known to behave as a charge transfer acceptor in a host donor molecule such as poly(vinylcarbazole) (PVK) [3] and tetrathiafulvalene (TTF) [4]. The crystal structure including molecular packing of DNF was first solved by Baughman [5]. His work showed that DNF belongs to a noncentrosymmetric orthorhombic space group $Pca2_1$ (point group C_{2v}) and has lattice parameters $a = 2.0998(5)$ nm, $b = 0.3793(1)$ nm, $c = 1.4252(5)$ nm and the number of unit formula $Z = 4$. It should be noted that there are significant differences in crystal structure between DNF and other known NFs. The structure consists of closely spaced stacks (about 0.34–0.35 nm spacing) of π-conjugated molecular planes and gives rise to a spontaneous polarization. So that the piezoelectricity, the first-order electro-optic effect and SHG are permitted in DNF crystal. On the other hand, unsubstituted 9-fluorenone [6] and other NFs such as TNF [7] belong to centrosymmetric structures, and the above-described properties are ruled out.

Until now, studying optical and electric properties of DNF crystal are very few despite the significant structure. In terms of above-described properties, only the SHG in powder form DNF was reported [8]. The main reasons of there being few reports are that not only were the electronic properties of DNF as a charge transfer complex acceptor mainly studied [9,10], but the hardly solubility of DNF in typical organic solvents make it difficult to prepare sufficient large optical quality single crystals by solution method.

Attempts to overcome these problems a sublimation technique was introduced to prepare DNF single crystal instead of the solution method. In this paper, the first results of crystal growth, structural characteristics, linear and nonlinear optical properties including refractive indices, second-order nonlinear optical coefficients and critical phase matching (CPM) condition.

2. EXPERIMENT

DNF single crystals were grown by a sublimation technique with the similar apparatus by Wagner *et al.* [11]. This kind of technique is known as the train sublimation for purification [11] and crystal growth [12] of organic materials. The starting material was a commercially available DNF (Tokyo Kasei inc.) and was sublimed at 280°C in a glass tube with an inner diameter of 15 mm. The vapor DNF was transported to the lower temperature region of the tube in a flow of purified nitrogen gas and re-crystallize. The temperature of the crystallization and growth region was about 250°C at the gradient of 5°C/cm. In order to separate impurities, the sublimation process was repeated several times using the grown crystals as the next source material and the last crystals were used for the following investigations.

The crystal structure was confirmed and the crystal axes direction within the single crystal was determined by the X-ray diffraction (XRD) measurements. (Rigaku RAXIS-RAPID and RINT TF-PC2)

The polarization transmission spectra were measured using thin plate-like crystals with flat surfaces. (Shimadzu, UV-3100) The refractive indices were determined using the spectra. The experimental results were confirmed from the viewpoint of molecular and crystal structure.

The second-order nonlinear optical properties were studied using the Maker fringe technique [14] which allows one to measure the second-order nonlinear optical (S-NLO) coefficients (d_{ii}), with acceptable accuracy. The fundamental light at 1064 nm of a Q-switched Nd:YAG laser was used. The coefficient is obtained by comparing the intensity of SHG between the DNF and the Y-cut quartz which is generally used as the reference material.

From the viewpoint of the usage for SHG, Type I and Type II CPM conditions were calculated by using the refractive indices. The effective S-NLO coefficient (d_{eff}) under the CPM conditions was also calculated.

3. RESULTS AND DISCUSSION

A. Crystal Growth

In the growth region of glass tube, the plate-like single crystals with dimensions up to $10 \times 5 \times 0.5\,\mathrm{mm}^3$ were grown from glass surface to inner

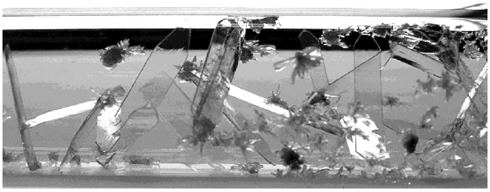

FIGURE 1 DNF single crystals grown by train sublimation technique in glass tube with an inner diameter of 15 mm.

space randomly, as shown in Figure 1. The prismatic ones with the almost same dimensions were coexistent. These crystals were colored in pale yellow and were optically clear.

When the first cycle was completed, a black stuff remained where the source material had been and a fluorescent yellow stuff deposited in the cooled region of which the temperature was under 100°C. The yellow stuff was considered to contain some fluorene derivatives. Both stuff were almost unidentified when the second cycle was done.

The XRD measurements showed that the crystal structure of the obtained single crystals is orthorhombic space group $Pca2_1$ (point group C_{2v}) with lattice parameters $a = 2.0999$ nm, $b = 0.37185$ nm, $c = 1.41674$ nm. The structure quite agrees with that described above [5]. The XRD measurements also showed that the crystallographic a, b and c axes are parallel to the thickness direction, the short and long edges of the wide face, as shown in Figure 2. The spontaneous polarization is directed along c-axis.

B. Linear Optics

Polarization transmission spectra for the incident light normal to bc-plane, the widest natural growth plane, and polarized parallel to b and c axes are shown in Figure 3. The cut-off wavelength, at which the transmittance fell to 50% is 429 nm and 438 nm for the incident light parallel to b and c axes, respectively. The absorption is considered to be caused by π-π^* transition [10]. The transparency region extends to about 3000 nm in the IR range while Figure 3 displays data in the range of 400 to 1900 nm.

Biaxial crystals show three different refractive indices along the dielectric principal axes. In orthorhombic crystals, the dielectric principal axes (X, Y, Z) correspond to crystallographic axes (a, b, c). Therefore, the

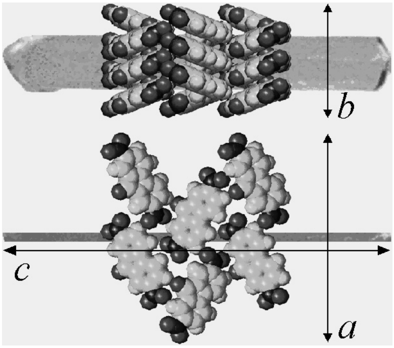

FIGURE 2 The crystal structure within the single crystal.

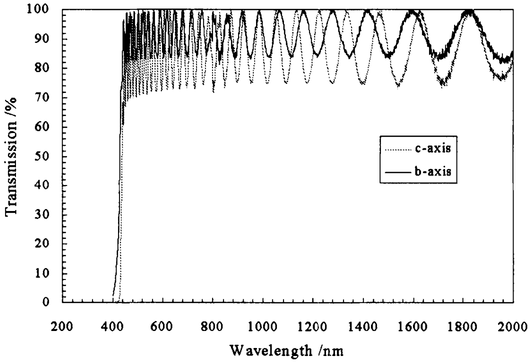

FIGURE 3 Polarization transmission spectra for the incident light polarized parallel to b and c axes. The solid lines show the reconstructed spectra using the optimized Sellmeier parameters.

principal refractive indices in the transparency region were determined using polarization transmission spectra as follows.

As shown in Figure 3, the interference fringes are superposed on the spectra in the transparency region. The spectra are considered to be almost ideal because the peak of fringes are just 100(±0.1)% without subsequent mathematical operation and the irregular changes of amplitude or cycle of fringes are unidentified. In this case, the spectra can be reconstructed using Fresnel coefficient to which proper refractive index dispersion curves are applied. The refractive index dispersion curves are known to be represented by a Sellmeier equation of the form $n^2 = A + B/(\lambda^2 - C) - D\lambda^2$, where λ is the wavelength and the A, B, C, and D are Sellmeier parameters. Therefore the refractive index dispersion curves can be determined by optimizing Sellmeier parameters and fitting the reconstructed transmission spectra to the measured ones.

The best fitted reconstructed spectra for the incident light polarized parallel to b and c axes by optimizing Sellmeier parameters of n_b and n_c, respectively, are shown in Figure 3. They are in good agreement with the measured ones and accuracy of n_b and n_c are considered to be sufficient. n_a was also determined by the same process, fitting to the spectrum measured for the p-polarized light at 40°, 50° and 60° angles of incidence. The Fresnel coefficients in those cases are given in a book [13]. The determined refractive index dispersion curves are shown in Figure 4. It shows that DNF is negative biaxial with $n_a > n_c > n_b$ and the birefringence is $n_a - n_b = 0.52$ at 532 nm.

The relation $n_a > n_c > n_b$ is consistent from the viewpoint of molecular structure and crystal structure because a, b, c axes lie almost parallel to the long and short axes of molecular plane and the stacking direction,

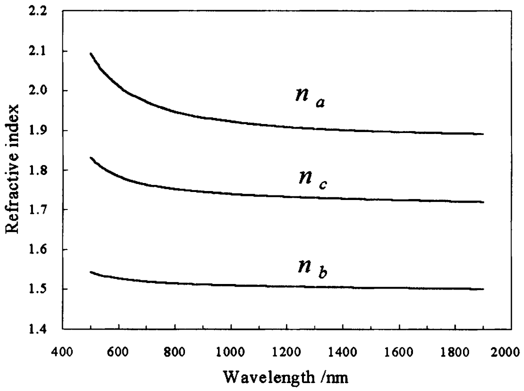

FIGURE 4 The refractive index dispersion curves determined by the optimized Sellmeier parameters.

respectively, and the electronic polarization induced by the light polarized parallel to each axis is considered to descend in this order.

C. Nonlinear Optics

Since DNF belongs to the orthorhombic crystal class C_{2v}, there are five nonzero components of the second-order nonlinear optical coefficient tensor, d_{15}, d_{24}, d_{31}, d_{32} and d_{33}. Under the Kleinmann symmetry condition, $d_{15} = d_{31}$ and $d_{24} = d_{32}$, then only three independent components are remained.

The Maker fringe technique was performed for the single crystals those were set so that the *c*-axis was parallel to the rotation axis and both the fundamental and the second-harmonic (SH) lights were polarized parallel to the rotation axis. Under the condition, the detected SH light contains the contribution of d_{33}. The Maker fringe pattern of a 120 µm-thick crystal is shown in Figure 5. The points and the solid line in the figure represent the measured data and the fitting line for determining the d_{33} value. The d_{33} value was calculated to be 7.5 ~ 8.5 pm/V for the seven samples with the thicknessof 45 ~ 120 µm by comparing the Y-cut quartz of which the effective coefficient $d_{\text{eff}} = 0.4$ pm/V. Therefore $d_{33} = 8$ pm/V is used in the following calculations.

The intensity of the SH light dependent on the polarization angle of the fundamental light were also measured for the crystals under parallel and crossed nicoled conditions. The fundamental light was kept normal to the *bc*-plane and the detected SH light contains the contribution of d_{33} and $d_{24} = d_{32}$. The $d_{24} = d_{32}$ value was calculated to be 0.36 pm/V by comparing $d_{33} = 8$ pm/V and was used in the following calculations. Unfortunately,

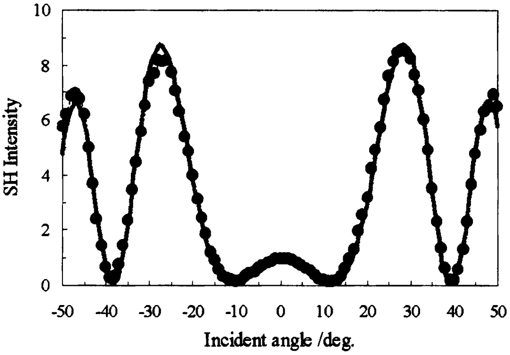

FIGURE 5 The Maker fringes of a 120 µm-thick crystal. The points and the solid line in the figure represent the measured data and the fitting line for determining d_{33}.

the $d_{31} = d_{15}$ value was not determined because both *ab*- and *ac*-planes are too narrow to measure the quantitative intensity of the SH light.

Type I and Type II CPM angles [θ, ϕ] were calculated using the determined refractive indices. Figure 6 shows the angles for the fundamental light at 1064 nm. The inset of the figure shows the definition of angle θ and ϕ. The figure shows both Type I and Type II CPM are possible in XZ-plane among the three principal planes. The calculated angles are [θ, ϕ] = [63.78°, 0°] for Type I and [θ, ϕ] = [37.83°, 0°] for Type II. Here the bored points in

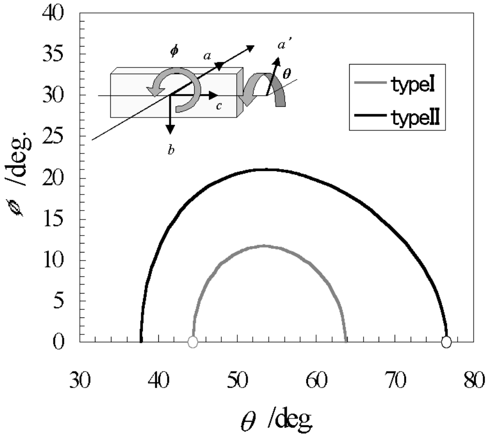

FIGURE 6 The calculated phase matching angles at the fundamental wavelength of 1064 nm.

the figure represent the conditions of $d_{\text{eff}} = 0$ and these conditions should be neglected.

The d_{eff} values under Type I and Type II CPM in XZ-plane are given by $d_{\text{eff}} = d_{32} \cos^2\theta + d_{31} \sin^2 \theta$ (at $\theta = 63.78°$) and $d_{\text{eff}} = d_{24} \cos^2 \theta + d_{15} \sin^2 \theta$ (at $\theta = 37.83°$) respectively. Both d_{eff} are independent of the diagonal coefficient d_{33} but dependent on the non-diagonal coefficients. The $d_{24} = d_{32}$ value is considered negligible, but the d_{31} value is sure to be larger than the d_{32} value and possible to be up to the d_{33} value with considering the relation $n_a > n_c > n_b$. It is noted that the molecules in typical organic crystals are coupled by relatively weak Van der Waals interaction and/or hydrogen bond, it is difficult to cut and polish in any wanted planes as well as to grow large crystals. From that point of view, the CPM in the principal planes are preferable to any other CPM conditions. In the matter of DNF, Type I CPM is more preferable to Type II because of the larger $\sin^2\theta$ value. Furthermore, DNF with the considerable contribution of non-diagonal components to d_{eff} is completely different from one-dimensional conjugated systems such as 2-methyl-4-nitroaniline that have only one dominant diagonal component.

In future, determination of the $d_{31} = d_{15}$ value and identification of the calculated CPM conditions were required.

4. CONCLUSION

In this study, sufficient large and good optical quality single crystals of DNF have grown. The crystals belongs to a noncentrosymmetric orthorhombic space group $Pca2_1$ and is negative biaxial with $n_a > n_c > n_b$ having a large birefringence with $n_a - n_b = 0.52$ at 532 nm.

The S-NLO properties were permitted under the symmetry and was investigated through the measurement of SHG. The S-NLO coefficients $d_{33} = 8\,\text{pm/V}$ and $d_{32} = d_{24} = 0.36\,\text{pm/V}$ were obtained. The CPM conditions were calculated and both Type I and Type II are possible in XZ plane among the three principal planes. Type I CPM in XZ-plane is considered to be preferable to any other CPM. In future, determination of $d_{31} = d_{15}$ and identification of the calculated CPM conditions were required.

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