비선형 광학적 소재인 Methyl-2-(2,4-dinitroanilino)propanoate (MAP)와 2-methyl-4-nitroaniline (MNA)의 혼합재료에 대한 결정성장 및 그 구조와 편광해석법의 적용

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Anisotropic Crystal Growth and Structure of Efficient Non-linear Optical Materials in the Adduct Between Methyl-2-(2,4-dinitroanilino)propanoate (MAP) and 2-methyl-4-nitroaniline (MNA) System, and Application of Ellipsometry for Its Material

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Introduction

Recently, the nonlinear optical properties of organic molecular solids have received considerable interest because of their very large optical nonlinearities and higher efficiency compared to the inorganic crystals[1]. They usually consist of a frame of conjugated double bonds, and electron-donating and electron-attracting substituents.

Of particular promise are the organic materials known for their efficient second harmonic generation (SHG)[1]. This is of present technological interest because GaAs | $Ga_{1-x}Al_xAs$ diode lasers resonate in the near-IR region (> 850 nm), are mass-produced at low cost, and are used in write-once, read-many optical data storage (compact discs, video discs). The need for greater data compression into the same storage space requires that the operating wavelength be shortened, to the visible or ultraviolet part of the spectrum. There are no practical light-weight lasers that operate in the 200 to 500 nm (UV to visible) region of the electromagnetic spectrum. Materials with high $\chi^{(2)}$, e.g. potassium dihydrogen phosphate (KDP)[2], or lithium niobate ($LiNbO_3$)[2], or the organic crystals 2-methyl-4-nitroaniline (MNA, Fig. 1)[4,5] or methyl-2-(2,4-dinitroanilino)-propanoate (MAP, Fig. 1)[3] can efficiently double the frequency of an input laser beam, say from 1064 nm to 532 nm, thanks to their high $\chi^{(2)}$ value.

Ellipsometry is an optical surface analysis technique for studying surfaces and thin films. The reflectivity of anisotropic materials, in particular, is interesting because many real materials material are optically anisotropic. A crystal such as a MAP:MNA material belongs to the monoclinic system is biaxial because there are two directions of propagation in which the birefringence disappear.

We present here the crystal growth and structure for the 1:1 adduct MAP:MNA, and application of ellipsometry for its material, which was obtained from two known

organic molecules, MAP[6] and MNA[4,5].

Experimental

MNA was obtained commercially (Aldrich Chemical, 97% purity), and was purified by the physical vapor transport method using argon as the carrier gas at 150-160°C. Orange-yellow single crystals of mixed MAP:MNA were grown by slow evaporation from solution using a 40:60 mixture of ethanol and ethyl acetate[7].

The crystal and molecular structure were determined by an Enraf-Nonius CAD-4F automated four circle x-ray diffractometer using Mo ($K\alpha$) radiation. The unit cell and the orientation matrix were found by a least-squares fit to 24 reflections in the range θ = 9-18°. The space group ($P2_1$) was determined by the systematic absence ool, l=odd. The structure was solved by direct methods. The H atoms were found on difference Fourier maps. The structure was refined by full-matrix weighted least squares, using anisotropic thermal parameters for all non H-atoms and isotropic thermal parameters for the H atoms, to a final weighted R index of 4.40% (unweighted R index 4.45%; 1783 observations, 346 parameters)[8].

The ellipsometer used for the measurement was the Auto-EL-III (Rudolph Research). Ellipsometric data (null measurements) for MAP:MNA were collected at both 70° and 60° incidence, as a function of 15° increments of the angle of rotation about a normal to the reflecting surface. Measurements were made in two zones, which corresponded to the two possible solutions for P (polarizer angle) and A (analyzer angle).

Results and Discussion

A stereographic illustration of the packing in the unit cell is given in Fig. 2[8]. The structure consists of sheets of MAP and MNA molecules that lie roughly in the (101) plane, and that stack approximately along [010]. The benzene rings of MAP and MNA are almost parallel to each other (the dihedral angle is only 4.41°), but are tilted with respect to the stack axis [010] by 23.44° (MNA) and 26.72° (MAP). The molecules are so stacked that the benzene C atoms are almost eclipsed; the amine group of MNA is below a nitro group of MAP (N7 almost eclipses N28); while the nitro group on MNA is below the aminopropanoate group nitrogen of MAP (N9 almost eclipses N18). The average of the ten intermolecular MAP...MNA non-bonded distances (< 3.7 Å). The crystal structure shows altering perpendicular π overlap between the almost eclipsed stacked aromatic rings of the MAP and MNA moieties, stacked at typical van der Waals distances. Since MAP is chiral (at atom C19), the structure is acentric. The packing seems to be dominated by π-π interactions between the MAP and MNA molecules (which may explain the color of the crystals, which may be due to a weak charge-transfer interaction between MAP and MNA), with some contribution from the localized hydrogen bond.

To observe the SHG efficiency[7], the crystals were crushed to a fine powder placed between two glass slides, and exposed to the 1064 nm laser beam from a pulsed Nd:YAG laser. Intense green light was observed from the powder indicating that the new material exhibited SHG with high efficiency. The intensity of the green light from this powder was compared to that of MAP and MNA powder

samples held between glass slides in a similar fashion. The powder SHG efficiency for the new material was observed to be the same as that of MAP, but less than that of MNA under identical conditions.

MAP:MNA is a biaxially anisotropic crystal because it is a monoclinic ($P2_1$) as given x-ray data. To obtain the optical constants (n_1, k_1, n_2, k_2, n_3, k_3) of MAP:MNA from experimental ellipsometric data, computer program for the 4 x 4 matrix technique is used[9]. The principal values of the real parts of the refractive index tensor for MAP are n_1 = 1.5078, n_2 = 1.5991 and n_3 = 1.8439 (at wavelength λ = 1064 nm), and n_1 = 1.5568, n_2 = 1.7100, and n_3 = 2.0353 at λ = 532 nm [10]. Two of the diagonal real values of the refractive index for MNA[5] are n_1 = 2.0 ± 0.1 and n_2 = 1.6 ± 0.1 at λ = 632.8 nm. The principal values of the refractive index tensor for MAP:MNA are approximately expected midway between values for the components of this 1:1 complex. Accurate optical nonlinearities and the refractive indices will be published.

Conclusion

Single crystal of the adduct between 1:1 methyl-2-(2,4-dinitroanilino)propanoate (MAP) and 2-methyl-4-nitroaniline (MNA) was grown from solution using a 40:60 mixture of ethanol and ethyl acetate. For the 1:1 MAP:MNA, the crystal data are: molecular formula $C_{10}H_{11}N_3O_6.C_7O_8N_2O_2$ (=$C_{17}H_{19}N_5O_8$), molar mass M_r = 421.37, monoclinic crystal system, space group $P2_1$, unit cell constants **a** = 6.9196(5), **b** = 7.673(8), **c** = 18.554(1) Å, β = 92.547(6)°, V = 984.1 $Å^3$ Z = 2, Dx = 1.422 gcm^{-3} λ(Mo Kα) = 0.71069 Å, R = 0.044 for 1783 observed reflections. A powder sample shows significant frequency-doubling intensity. The principal values of the refractive index tensor for MAP:MNA are approximately expected midway between values for the components of this 1:1 complex.

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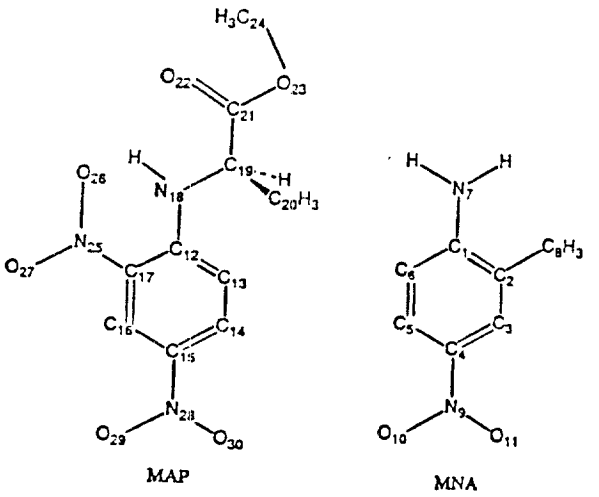

Fig. 1. Chemical structure of MAP and MNA.

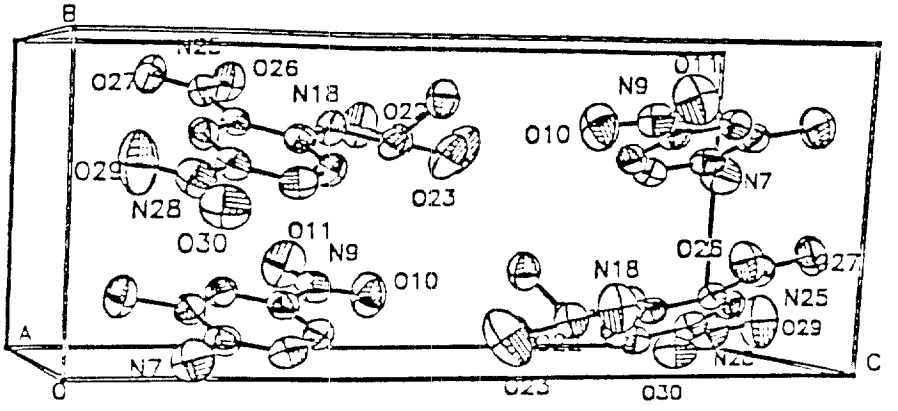

Fig. 2. Stereoscopic drawing of the molecular packing within the unit cell, projected onto the (011) plane. Hydrogen atoms are omitted.