The Growth and Linear-Electro-Optic Effect of Molecular Crystal: Hexamine(CH_2)_6 N_4

メタデータ	
	言語:
	出版者: 琉球大学理工学部
	公開日: 2012-02-28
	キーワード (Ja):
	キーワード (En):
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URL	http://hdl.handle.net/20.500.12000/23493

The Growth and Linear-Electro-Optic Effect

of Molecular Crystal: Hexamine $(CH_2)_6 N_4$ **

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Abstract

The crystal growth, optical properties, and electro-optic coefficients of hexamethylene-tetramine (HMT), $(CH_2)_6 N_4$, are described.

Crystals were grown from vapor phase by controlled sublimation in an electric furnace and from alcoholic solution. Crystals were transparent from 2200 Å with the measurement in the range of ultraviolet and visible spectrum, and showed dodecahedral habit exhibiting a distinct {100} natural growth faces. Crystalline index of refraction at 20°C was measured using microscope to be 1.57 at wavelength of 5893 Å.

The electro-optic coefficient γ_{41} was found to be $0.68 \sim 1.2 \times 10^{-10}$ cm/V for 5893 Å at room temperature. The applied voltage required to produce a phase difference of π, or one-half wavelength is about 63 KV for the crystal grown from alcoholic solution. The wavelength dependence of the electro-optic coefficients, the half-wave voltage, and the conditions for the crystal growth are discussed. Nonlinear susceptibility and the second harmonic coeffient are estimated to be 0.6 $\times 10^{-10}$ cm/V and the order of 10^{-10} cm/V, respectively.

1. Introduction

The electro-optic effect may be regarded as a change in optical dielectric tensor of crystal upon the application of a static electric field. When this change is linear in the applied field strength, it is called the linear electro-optic effect or Pockels effect.[1]

The linear electro-optic effect in crystals of class V_d such as ADP and KDP can be used for modulaling or shuttering light beam, but natural birefringence of crystals limits angular aperture. If crystals of class T_d are available, this difficulty is overcome, and the construction of a light modulator with a large useful angular aperture becomes possible.

Recently, the rapid development of quantum electronics has produced a demand for new materials that exhibit nonlinear optical effects[3] such as second harmonic generation, electro-optic effect,[2] multiphoton absorption, parametric oscillation, stimulated Raman and Brillouin scattering. In particular, linear electro-optic effect is very useful and convenient for the laser modulation and shuttering to deal with.

The effect may be observed in any of the 20 crystal symmetry classes exhibiting piezo-electricity. The general phenomological theory of the effect was given by Pockels.[1] More detailed treatments were given by Billings, Carpenter, West,[4] and Namba.[5] The symmetrical conditions which characterize the electro-optic effect in various crystal classes have been summerized by Vlokh and Zheludev.[6]

In an ionic crystal, a portion of electro-optic effect has been attributed to the

lowering of the crystal symmetry by piezo-electric strain.

In contrast to the extensive literature on the linear electro-optic effect in ionic crystals, little has been reported on that in molecular crystals.

In 1963, McQuaid[7] found that HMT possesses a linear electro-optic effect. It is the purpose of this paper to prepare a single crystal of HMT and determine the electro-optic coefficients as a function of wavelength in visible spectrum at room temperature, and then to obtain the half-wave voltage required to produce the phase difference of π.

2. Experimental results and discussion.

Single crystals can be grown either from aqueous or alcoholic solution or from the vapor phase.[10] Crystal grown from solution sometimes contain solvent and both solution and vapor crystals show strain pattern when viewed through crossed polarizers.

Crystals grown from alcoholic solution at constant temperature are better than the ones grown at changing temperature. Solubility of HMT in methanol solution is determined experimentally to be given by the formula $S = (0.2t + 5/2)$ g/100 cc.

Growth temperature was controlled to $30 \pm 0.05°C$ or better. The crystal obtained by this method is about 4 x 5 x 9 mm³ in dimension, and tends to show distinct (100) face. Solvent could be included in the crystal, which is inferred from the absorption spectrum of near infra-red that can be identified with that of CH stretching vibration modes.

Hexamine was the first organic crystal structure to be solved by X-ray studies. The crystal structure is $I\bar{4}3m$(bcc) with cubic edge a= 7.02Å. This structure has been verified by many workers. The molecular structure of HMT is similar to that of adamantane. Schaffer has proved that the molecular structure in crystal is distorted as compared with the undistorted cage structure in the gas. He pointed out that the distortion is accounted for by the formation of weak intermolecular hydrogen bonds between carbon and nitrogen atoms on adjacent molecules.

The lattice constant is determined by reflection spectrum of X-ray measurement to be 7.0Å at room temperature, and therefore, we identify the face of the sample with the (110) face and concluded that single crystal has been grown.

The crystalline optic transmission spectrum of HMT is obtained at room temperature in the wavelength range from 2000 A to 50μ by a JASCO and HITACHI spectrophotometers. (Fig.3). The crystal is transparent for the wavelength ranging from 1.6μ to slightly below 0.22μ.(Fig1,Fig2). The strong absorption near 0.22μ is attributed to the excitation of nitrogen nonbonding electrons. (Fig.1). Weak absorption in the range from 2.2μ to 2.6μ is due to the first overtone of CH stretching vibrations, and water hydration. The spectral responce of molecular crystals is close to that of isolated molecule due to the weak intermolecular coupling characteristic of Van der Waals binding.[8]

The crystalline index of refraction at 20°C was measured using polarizing microsope to be 1.57 at 5893 Å. One of the natural growth faces {110} , which is identified with reflection spectrum of X-ray study of a crystal of HMT, was polished with filter paper soaked with methanol. Electrodes with a separation of 3 mm were attached on the crystal surfaces of (110) with an air-dried silver paint. The crystal was
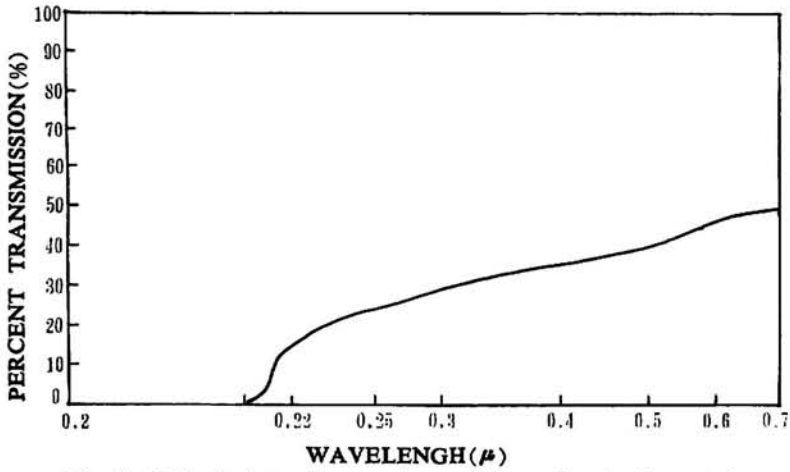
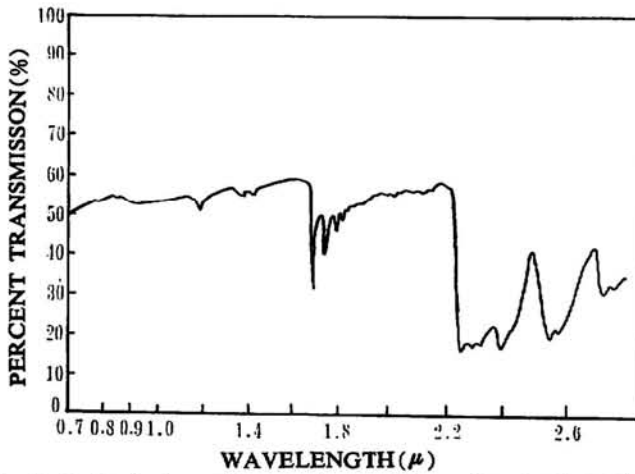Fig. 1. Optical absorption spectrum of hexamine single crystal.

Fig. 2. Optical absorption spectrum of hexamine single csystal.
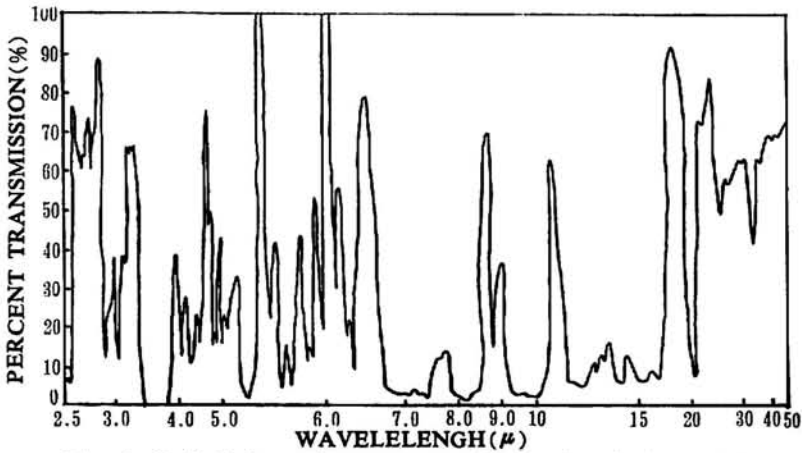

Fig. 3. Optical absorption spectrum of hexamine single crystal.

placed between crossed Glan-Thompson polarizers in the beam of laser or Hg-lamp source. The increase in light level with applied electric field was detected by DuMont 6292 photomultiplier and compensated dy Babinet-Soleill compensator until the light vanished.
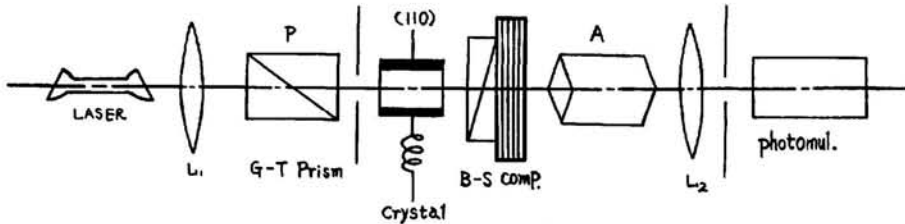

Fig. 4. Optical system for retardation measurement.

Retardation or phase difference for HMT sample was measured by Babinet-Soleill

$$\delta = \frac{2\pi}{\lambda} \cdot \frac{l}{d} \cdot n_o^3 \gamma_{41} V$$
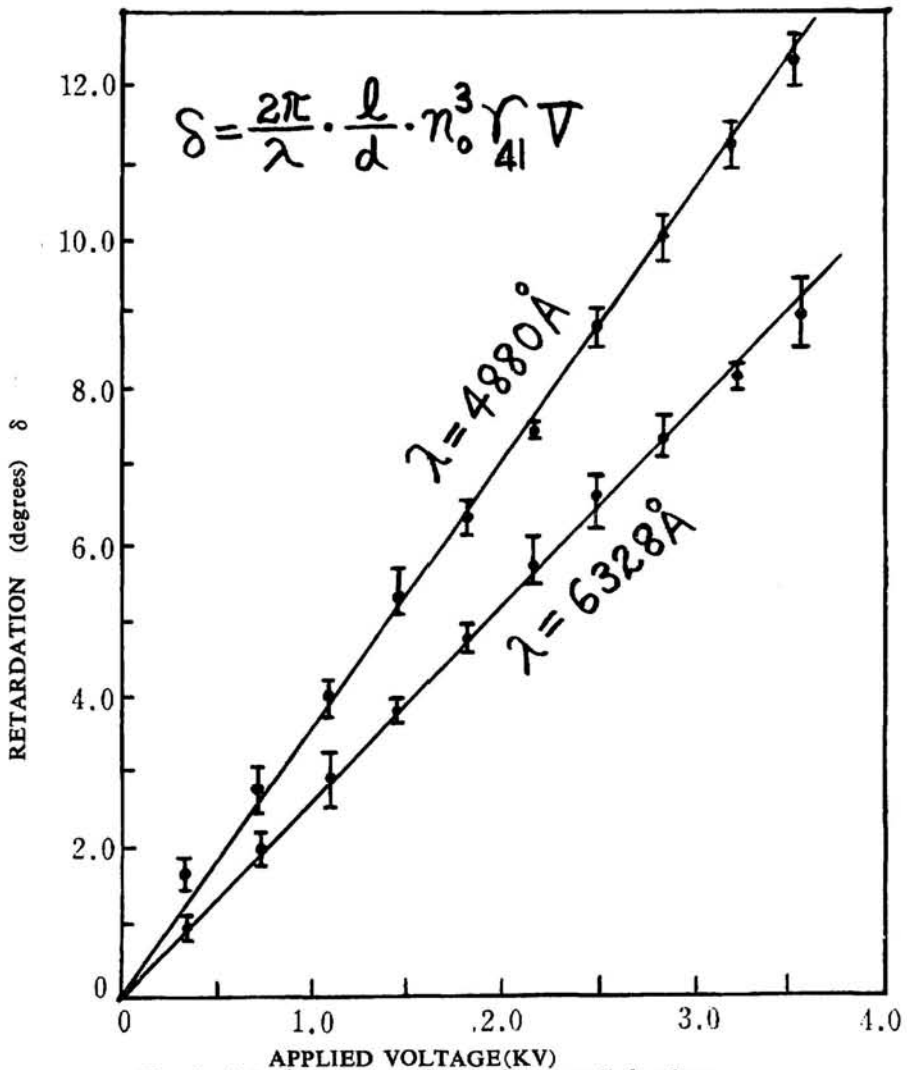
Fig. 5. Retardation per unit length vs. applied voltage.

compensator method with applied electric field in the (100) direction and light travelling
in the ($\bar{1}$10) direction. Optical system used for retardation measurement is shown in Fig.
4. Results are shown in Fig 5. The values of birefringence $n_0^3\gamma_{41}$, half-wave voltage$V\frac{1}{2}$,
and the wavelength dependence of the linear electro-optic coefficients γ_{41} are shown
in Fig. 6. The results obtained show that γ_{41} is $1.07 \sim 1.17 \times 10^{-10}$ cm/V and constant
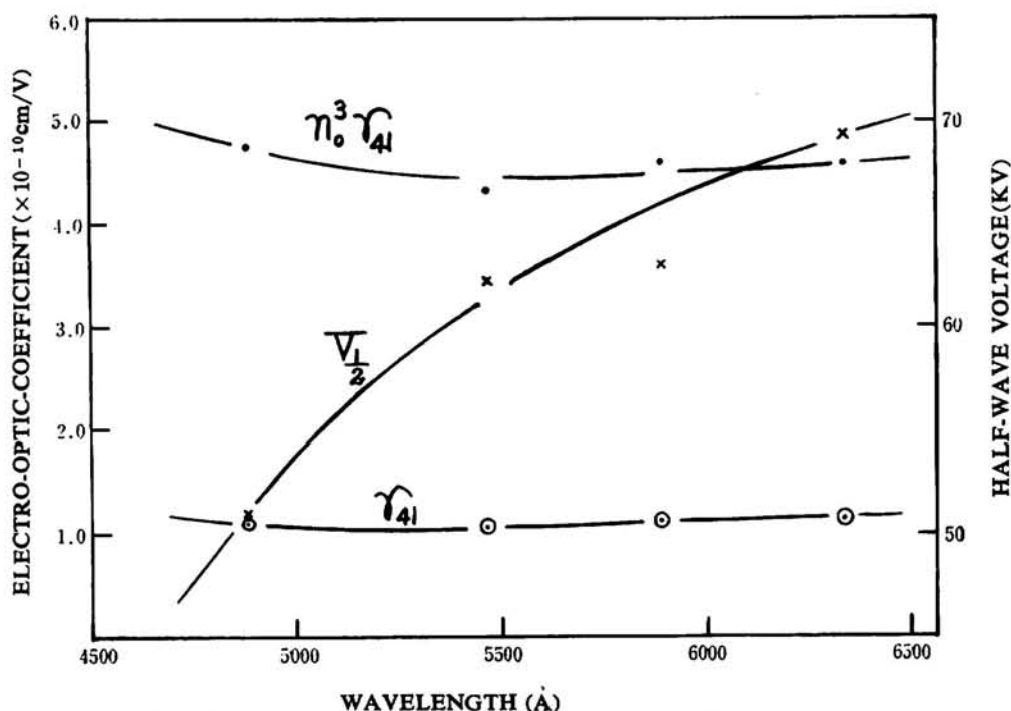over a rang of visible light[9].

Fig. 6. Electro-optic coefficient, birefringence, and half-wave
voltage of hexamine single crystal vs. wavelength.

The corresponding half-wave voltage at 6328 Å (He-Ne laser) and 4880 Å (Ar$^+$
laser) are 71 KV and 52 KV, respectively.

3. Conclusion

Single crystal has been grown from solution and vapor phases. It is seen from
our observation that crystals grown from the solution are much larger than the ones
grown from the vapor, but that they seem to include in them solvent. The crystal has
no absorption in the range of visible and near infra-red light. It is concluded that the
better condition of temperature for single crystal growth in solution is 30°C and that
this condition, however, is affected by the rate of evaporation of solvent and also
slightly by the humidity of the atmosphere.

Little variations of the linear electro-optic effect and the wavelength dependence
of birefringence are found in visible light, and these two may considered to go in parallel.

The half-wave voltage increases with the wavelength. These indicate that the light modulation at visible light is sufficiently possible and more easier to deal with the mechanism of appliedfield than that of near infra-red.

Nonlinear susceptibility of HMT obtained from the experimental result of Ar$^+$ laser at 4880 Å may be estimated to be 0.6×10^{-10} cm/V at room temperature, and the order of this value suggests that the second harmonic coefficient of HMT crystal excited by the Q-switched laser could take sufficiently large value of the order of 10^{-10} cm/V.

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