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Short Notes

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Growth of o-Dicyanovinyl Anisole (DIVA) Crystal in Organic Solvents and its Characterization

1. Introduction

The organic non-linear optical (NLO) crystal o-dicyanovinyl anisole (DIVA) has been paid more attention in the application for frequency doubling of diode laser due to its large phase-matching second harmonic generation (PMSHG) coefficient and good transparency in the visible-IR region (WADA, GROSSMAN). The effective PMSHG coefficient (d_{eff}) is 4.9x 10^{-9} esu, about 40 times of d_{11} of α-quartz (WADA, YAMADA). Some methods of growing DIVA crystals have been reported (SASABE, WADA), but there is no detailed description so far. In this paper crystal growth habits of DIVA in several organic solvents such as acetone, ethanol, ethylacetate are described. Perfect large DIVA single crystals have been grown from acetone or ethylacetate by solution growth technique including low-temperature and evaporation methods. The mechanism of growth is discussed. The grown crystals are characterized.

2. Growth of DIVA crystal in organic solution

In order to investigate the crystal habit of DIVA, various organic solvents were tried. Solubility and crystal habits of DIVA in several solvents are listed in Table 1. In general, DIVA can be dissolved in most of the organic solvents, e.g. alcohol , acetate, ethyl acetate, but its crystal habits and crystal quality are different. In its alcohol solution DIVA crystallizes in particular form, and the crystal quality is poor. It has been found that its crystal habits and crystal quality in acetone solution and in ethyl acetate are good. It appears in platy forms in acetone and has a good transparency. In ethyl acetate it appears in rhombs. These two crystal forms are shown in Figures 1a, b. The experiments show that the solubility of DIVA in acetone is larger than in ethyl acetate, and the solubility increased with increase in temperature in both cases. Solubility curves of DIVA in acetone and in ethyl acetate are shown in Figure 2, respectively. As seen from this figure, the DIVA crystal is

appropriate to be grown from acetone solution or ethyl acetate solution by the low-temperature method. Other solvents, however, such as ethanol, and chloroform are not very suitable for bulk growth. The DIVA single crystals, having a good quality, with dimensions up to 17x14x5 mm^3, were obtained by this method. The growth temperature range in acetone was 30-25°C, in ethyl acetate 33-28°C. The rate of temperature reduction was kept at 0.05°C/day under control, and a temperature fluctuation of less than 0.02°C was allowed. Figure 3 shows the photograph of crystals by successful growth. The faces of the crystal in Figure 3 were determined by X-ray diffraction as shown in Figure 4.

Table 1
Crystal habits of DIVA in several organic solvents

solvents	solubility 30°C g/100ml sol.	crystal form	crystal transparency
acetone	45	platelet	good
ethyl acetate	39.5	rhomb	good
i-Buthyl alcohol	26	staple	fairly good
alcohol	25	particular	poor
chloroform	16	slice	fairly

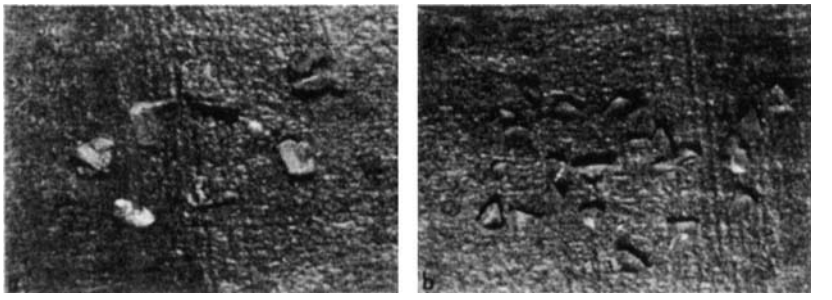

Fig. 1. Crystal forms of DIVA. a) in acetone
b) in ethylacetate

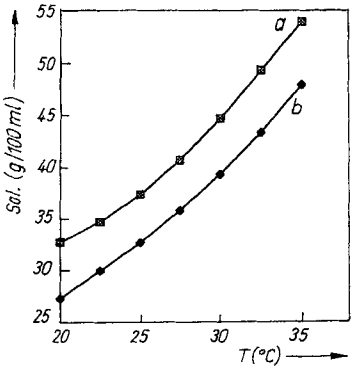

Fig. 2. Solubility curves of DIVA: a) in acetone b) in ethylacetate

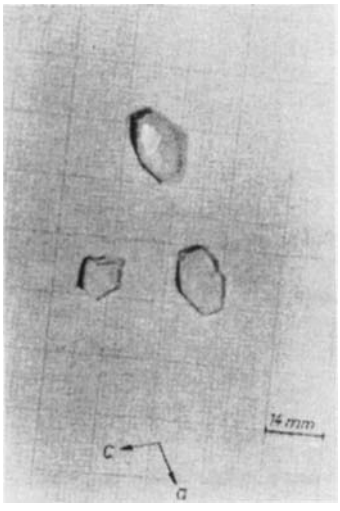

Fig. 3. As-grown single crystals of DIVA

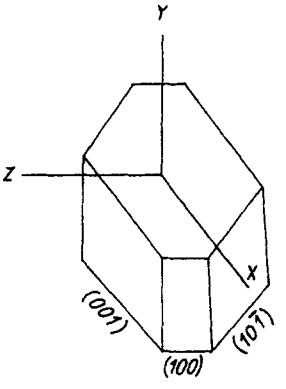

Fig. 4. Schematic drawing, showing the different faces of a DIVA crystal

In addition, an evaporation method was also suitable for DIVA growth from acetone solution. DIVA saturated acetone solution containing a seed at about 30°C was put into a specially designed growth apparatus, with the seed growing for two or three weeks and a proper control of solvent evaporating by a temperature and air current. A good quality crystal with the size 15x12x5 mm^3 has been obtained.

3. The transmission spectrum of grown DIVA crystal

The optical transmission of DIVA crystals has not yet been reported. In our experiment, the optical transmission spectrum of DIVA has been measured in a Hitachi UV-365 spectrometer. 3 mm thick grown DIVA crystals were used without any pretreatment. The [010] direction is used as the passing - light direction. The result is shown in Figure 5.

The cut-off absorption wavelength of DIVA is 420 nm. There is a good transparency from 450 nm to 1650 nm (transmission above $\sim$ 60%). A better transmission for DIVA may be expected, if the crystal is processed well.

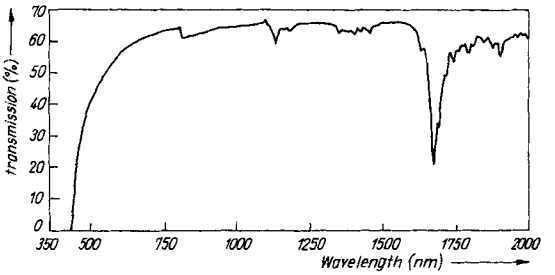

Fig. 5. The transmission spectrum of grown DIVA crystal

4. Result and discussion

The crystal habits of DIVA in several organic solvents have been investigated. It shows a good crystal habit in acetone and in ethylacetate. The crystals have been grown successfully from these solutions. It is noted that, as shown in Figure 2, the solubility of DIVA in acetone is high and the supersaturation is difficult to control with low-temperature growth. The higher the growth temperature, the larger the solubility of DIVA, and the colour of the growth solution gets dark. Contrariwise the solubility of DIVA in ethyl acetate is not large enough, but polycrystals were easy to form during growth. Larger crystals were difficult to grow in this case.

The particular habits of growth of the DIVA crystals in organic solution, especially in acetone solution, demonstrates its special crystal structure. Figure 6 shows the projection of DIVA molecules in the crystal along the c-axis. From this figure we note that the molecules are hold head to tail along the crystallographic b-axis, but the molecules are packed layer upon layer along [110] or [$\bar{1}$10], and the molecules are linked with each other by the cyano group of one molecule and the methoxy group of the next along the a-axis. Thus the crystals usually show plate-like forms (WANG).

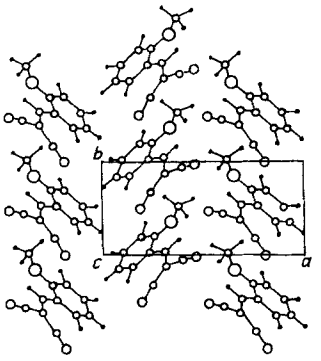

Fig. 6. The projection of DIVA molecules in the crystal along the c-axis

It can be stated that the DIVA crystals with good optical quality can be grown from acetone solution or ethyl acetate solution by solution growth techniques including low-temperature and evaporation methods. The optical transmission spectrum of grown crystals shows that the cut-off absorption wavelengh is 420 nm, indicating that the DIVA crystal will be a promising frequency doubling material for semiconductor laser.

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