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Growth of Single Crystals of meta-Nitroaniline and the Evaluation of its Electro-optic Properties

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Single crystal boules of meta-nitroaniline of good optical quality have been grown. Meta-nitroaniline exhibits a strong linear electro-optic effect, has a low refractive index and low permittivity, making it attractive for use in high-speed electro-optic modulators and deflectors.

1. Introduction

The purpose of the investigation reported here was to look into the electro-optic behaviour of materials showing a predominantly electronic polarisability. The interest centred around the linear electro-optic (Pockels) effect and the requirement for a material to show this is that it be non-centrosymmetric. There are several meta-disubstituted benzenes which belong to the non-centrosymmetric class mm2 [1]. Meta-nitroaniline [2] exhibits a rather convenient set of physical properties and was chosen for a detailed examination.

2. Crystal Growth

Crystals were grown by two methods; from the melt and by sublimation. In both cases, zone-refined (twenty passes) starting material was loaded into Pyrex glass capsules, degassed by pumping at around 110° C and sealed off in the capsules at a pressure of less than 10^{-2} torr. Melt-grown crystals were obtained using a simple Bridgman technique. Better results were obtained by a related technique where a capsule containing the molten charge and a small seed was placed in a thermostat at $\sim$ 1° C below the melting point of meta-nitroaniline. The charge solidified over a period of a week, the products being boules containing up to ten crystals, with single crystal regions of $\sim$ 1 cm^3. The crystals were heavily crossed by cleavage planes. It was also thought that the large volume reduction on solidification precluded the easy growth of meta-nitroaniline from the melt, and this approach was abandoned.

Crystals of far better quality and larger size were grown by sublimation just below the melting point where the vapour pressure of meta-nitroaniline is 0.66 torr. The experimental procedure was to seal approximately 30 g of meta-nitroaniline in a capsule under "vacuo". The capsule was 20 cm long and 1.6 cm internal diameter and terminated in a conically tapered seal. The capsule was suspended via a brass rod into a thermostatic bath which was maintained $\sim$ 1° C above the melting point of meta-nitroaniline, the brass rod acting as a heat leakage path. The method described is similar to that of Swets and Jorgensen [3]. On withdrawal, nucleation occurred in the tapered part. Several attempts had to be made before only one single seed was achieved. Further withdrawal led to growth. The growth rate, typically 0.1 mm h^{-1}, was adjusted by the rate of withdrawal, to keep the growth interface smooth and rounded. After growth, there was difficulty in removing the boule from the capsule as it showed a tendency to adhere to the glass walls. This difficulty was removed by using a thin PTFE liner or silating the inside of the capsule using the method of Datt *et al* [4]. Fig. 1 shows a typical vapour grown boule, which has one almost vertical cleavage; meta-nitroaniline shows perfect cleavage along the (010) plane.

At fast withdrawal rates the growing interface became pocked and reticular. It was thought that

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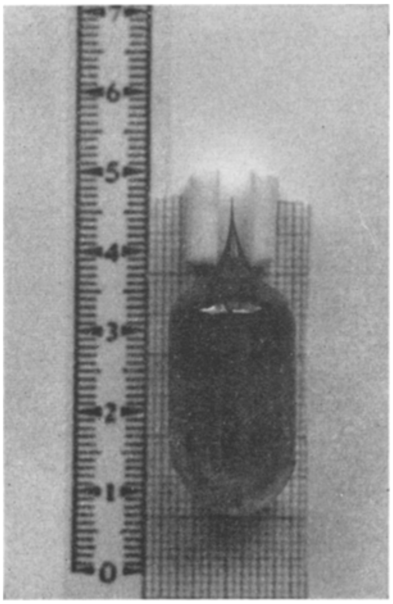

Figure 1 A vapour-phase grown boule of meta-nitroaniline (the numbered scale is in cms).

this was associated with the onset of "vapour constitutional supercooling" as propounded by Reed and LaFleur [5] for growth from the vapour. However, close scrutiny of the system, including some revealing experiments on growth from a supercooled source, suggested an alternative limitation. Details will be published later.

3. Physical Measurements

The linear electro-optic effect in meta-nitroaniline was investigated using a He-Ne laser at 0.6328 μm and a standard amplitude modulation technique. As expected, the largest effects were found when the electric field was applied along Z, the polar axis. Measurements were made on thirty-six different crystals and a summary of the results are given in table I. The results are expressed in terms of the half-wave voltage, $V_{\lambda/2}$, the voltage required on a unit cube crystal to achieve 100% modulation of the transmitted light.

No quantitative explanation of the variations of half-wave voltage is attempted here. However, all specimens were examined under a microscope with crossed polarisers and slices exhibiting uniform extinction yielded low half-wave voltages while others showing low angle grain boundaries gave higher values. The lowest half-wave voltage of 5.5 kV was observed for the transverse effect in the last vapour grown crystal with the light transmitted along the X axis and the electric field in the Z direction. Improved crystalline perfection may lead to lower half-wave voltages. The variations observed were much smaller than those reported by Fay [7] for the tungsten-bronze and perovskite-oxide families or those collated by Lee [8] for hexamethylene tetramine, another molecular crystal, where the span of values exceeded an order of magnitude.

An attempt was made to measure the dispersion of $V_{\lambda/2}$ as a function of wavelength. A monochromated white-light source was used over the range 0.55 to 0.7 μm but the intensity of light available at any one wavelength was very low resulting in a large uncertainty in the measurements, especially where the crystal absorption was considerable. However, in spite of this, a dispersive effect was noted as shown in fig. 2.

The permittivity at 3 kHz and the coefficients of linear expansion were measured along the three crystal axes and the results are given in table II.

4. Conclusions

The results on meta-nitroaniline show that materials of predominantly electronic polaris-

TABLE I Half-wave voltages, $V_{\lambda/2}$, for meta-nitroaniline.

Direction of— light*	field	$V_{\lambda/2}$ for melt-grown crystals (kV)		$V_{\lambda/2}$ for vapour-grown crystals (kV)	
		Average	Minimum	Average	Minimum
X (transverse)	Z	9.5 (of 4 crystals)	8.4	8.9 (of 25 crystals)	5.5
Y (transverse)	Z	19.5 (only 1 crystal)	18.9	17.6 (of 8 crystals)	10.7
Z (longitudinal)	Z	25.0 (of 2 crystals)	24.0	20.4 (only 1 crystal)	20.4

*In every case, the incident light was polarised at 45° to the other two crystals axes.

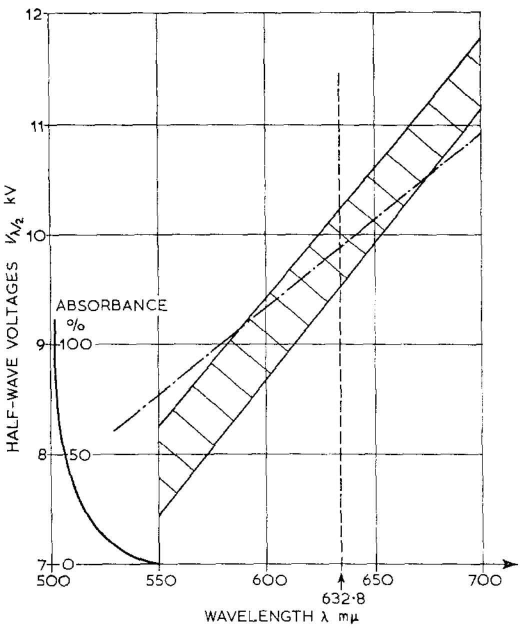

Figure 2 Graph of half-wave voltage against wavelength.

TABLE II Permittivity and coefficients of linear expansion of meta-nitroaniline.

$\epsilon_{11} = 3.9$	$\alpha_{11} = -40 \times 10^{-6}/°C$
$\epsilon_{22} = 4.2$	$\alpha_{22} = 150 \times 10^{-6}/°C$
$\epsilon_{33} = 4.6$	$\alpha_{33} = 108 \times 10^{-6}/°C$

ability can exhibit useful electro-optic properties. Unlike most electro-optic crystals, meta-nitroaniline combines low permittivity with good electro-optic behaviour. This, together with its easy growth into large single crystals, makes it attractive for many practical applications, such as digital deflectors for fast access large scale memories.

It is stressed that meta-nitroaniline is only a representative member of a very large family of materials [9]. Further search in this area is likely to prove fruitful.

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