Molecular Nonlinear Optical Materials [and Discussion]

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Molecular nonlinear optical materials

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[Plate 1]

Some organic crystalline solids that comprise highly polar molecules and that form non-centrosymmetric crystal structures exhibit second-order nonlinear optical properties and laser-damage thresholds that are potentially superior to those of currently available inorganic systems. This realization has led to a search for organic materials with improved properties and also to the consideration of organic crystals as active components in optical and optoelectronic device systems. Empirical and theoretical attempts have been made to predict novel molecules, which when synthesized might form, or be engineered to form, non-centrosymmetric crystals of even greater potential than the known systems. In parallel, efforts have been made to grow high quality, optically perfect, single crystals for the evaluation of the optical properties and device potential of this class of material. Data obtained on the resulting range of materials and crystals serve to confirm this potential.

1. Introduction

The fast-growing development of optical communication systems has stimulated the wider search for materials with highly nonlinear optical properties capable of forming the basis for devices for the efficient processing of optical signals.

Materials with nonlinear electro-optic properties have a role in modern optoelectronics that is analogous to that of nonlinear electronic circuit elements in conventional electronics. Typical functions of such elements are to modulate carrier waves, amplify and rectify signals and act as very fast switches.

2. Nonlinear optics

When electromagnetic radiation passes through a substance, the oscillating electric field, E, of the radiation polarizes the material and induces an oscillating electric dipole in the medium. The induced dipole per unit volume or polarization, P, is approximately linearly proportional to the applied field,

$$P \approx \epsilon_0 \chi_1 E, \tag{1}$$

where ϵ_0 is a universal constant (introduced to maintain a consistent system of electrical units) and χ_1 is the linear electric susceptibility.

Nonlinear effects arise from contributions to P which depend on higher powers of E,

$$P = \epsilon_0[\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \ldots]. \tag{2}$$

The odd terms in this expression, in which for simplicity the directional properties of the two vectors are ignored, contribute to the polarization of all materials. The values of the even coefficients χ_2, χ_4, etc., are restricted by a symmetry requirement. Non-zero even-order

[55]

coefficients are found only in crystals with non-centrosymmetric (acentric) space groups. In amorphous solids, liquids and gases and in solids in which the molecules are related by a centre of symmetry, the even terms are always zero.

The higher-order parameters only become usefully effective where they are significantly larger than is normally found. Hence, the search for materials in which they have exceptionally high values. The theme of this article is concerned with the identification and preparation of organic crystalline materials where χ_2 is unusually large.

Reference will be made to two particular nonlinear effects; the linear electro-optic effect or Pockels effect through which the refractive index of a material varies with applied electrical field, and second-harmonic generation (SHG) where irradiation of the solid with light of one frequency results in the emission of light of double that frequency.

There is a demand for materials that carry out this frequency conversion in a more efficient manner than currently available materials and that also are more physically and chemically stable under high-power incident laser irradiation. Also, for materials that undergo significant changes in refractive index under fields considerably less than the several thousand volts per centimetre required by currently used materials.

In the search for suitable materials with strong nonlinear responses attention has focused on organic materials for several reasons. Although examined for this type of behaviour a number of years ago, these examinations were restricted to materials of low performance (e.g. hippuric acid (Orlov 1966) and benzil (Gott 1971)) some of which were difficult to prepare in forms suitable for detailed evaluation. More recent appraisals have demonstrated that there were available organic materials such as urea (Halbout et al. 1980) and 2-methyl-4-nitroaniline (Levine et al. 1979), which show considerably improved performance over inorganic materials and which have unique optical properties. These observations have led to the wider examination of organic materials that confirmed their efficiency and also showed that they promised to give much higher damage thresholds for laser irradiation than inorganic materials (Chemla & Zyss 1987). Further impetus to this developing programme was given by the additional potential of organic molecules that if the molecular basis of the effect could be defined, then theoretical predictions might be possible to define molecules of much higher potential performance that could be synthesized and evaluated.

3. The origins of nonlinear behaviour in organic materials

Organic substances form molecular crystals, in which the molecules preserve their individual identity and are bound together by weak intermolecular (dispersion) forces. The crystal properties should therefore be the sum of the molecular properties.

In treating the response of the crystal to an external electric field, this principle has to be modified to allow for the effect of the internal field. The correction can be made through the well-known Clausius–Mossotti (Lorentz–Lorentz) or Onsager formulae, but greater precision has been achieved in molecular crystals by using lattice dipole sums calculations. This technique has recently been applied to nonlinear response functions by Munn and collaborators (Munn 1988).

Given that the connection between the crystal response and the molecular response to an external field can be established by such methods, the first step in looking for useful systems is to identify molecules with large nonlinear responses.

The molecular parameters analogous to the susceptibilities of equation (2) and from which the latter originate, are the linear polarizability (α) and the hyperpolarizabilities (β, γ, etc.). The dipole moment induced in the molecule by a field is,

$$\delta\boldsymbol{\mu} = \alpha E + \beta E^2 + \gamma E^3 + \dots . \tag{3}$$

(The tensor properties of α_{ij}, β_{ijk}, γ_{ijkl}, etc., are ignored for the purposes of this discussion.)

The first molecular hyperpolarizability (β) gives rise to second-order nonlinear effects, particularly the linear electro-optic effect and SHG. As for the bulk solid, molecular second-order effects depend on a lack of a centre of symmetry and β is only non-zero for acentric molecules. Second-order effects are the strongest nonlinear effects, when they occur. Let us consider the underlying reasons for the large values of β that occur in certain organic compounds.

Firstly, note that there is a connection between the existence of low-energy excited states in molecules and high polarizabilities of all orders. This can be seen from simple classical mechanics if a transition frequency is identified with a classical resonant frequency. If a spring has a low resonant frequency it means that it distorts easily (if the force constant is k, then the frequency $\nu = \frac{1}{2}\pi\sqrt{(k/m)}$). Also, as the frequency of the applied force approaches the natural resonance frequency, the amplitude of the motion gets progressively larger for the same field strength and therefore the polarizability is increased. In molecular terms this increase is described as preresonant enhancement.

To find the criteria for a large β we must also ask what it is that determines the 'effective' non-centrosymmetric characteristic of the molecule. Not all forms of asymmetry are effective. For example, a methyl (sp³ bonded) substitution on benzene does little to increase β from zero. To be useful a substituent group that breaks the symmetry must do so in such a way as to affect the low-lying excited state with which the nonlinearity is associated and hence the electronic distribution in the molecule. It is, therefore, at least reasonable that asymmetry on excitation to this state should be the relevant factor. In fact, it is the quantity, $\mu_n^0 - \mu_g^0$, the change in permanent dipole on excitation from ground to excited state, which is the appropriate measure of the lack of a centre of symmetry. This quantity is always zero for centrosymmetric molecules.

Second-harmonic generation in organic molecules is often discussed in terms of a two-state model (g is ground state, n is excited state) from which the formula,

$$\beta = \frac{3\hbar^2}{2m} \frac{f_{gn}\,\epsilon_n(\mu_n^0 - \mu_g^0)}{(\epsilon_n^2 - \hbar^2\omega^2)\,(\epsilon_n^2 - 4\hbar^2\omega^2)}, \tag{4}$$

can be derived. ϵ_n is the excitation energy and f_{gn} is the oscillator strength for the transition, $g \to n$, which measures the strength of the coupling of the external field to this transition. The factor $\mu_n^0 - \mu_g^0$ is present and the denominators indicate that there will be preresonant enhancement when either or both ω or 2ω approach the transition frequency. In fact only the latter can be used, because if ω were near to resonance, 2ω would usually be in a region of high absorption.

Consideration of these demands leads to the identification of intramolecular charge-transfer molecules as having potentially large nonlinearities. The prototype is 4-nitroaniline. The amino group donates electrons to the delocalized π system, the nitro group accepts electrons from the system. In the ground state the amino end of the molecule is already positive, but on excitation of the most intense transition in the electronic absorption spectrum there is a further

large transfer of electrons from the amino to the nitro end of the molecule. For this transition, $\mu_n^0 - \mu_g^0 = 8$ debye (1 debye $\approx 2.7 \times 10^{-29}$ C m). The absorption band is at 320 nm. There is therefore some preresonant enhancement (amounting to a factor of 2 or so in β) when 1.064 μm YAG laser light is doubled to 532 nm.

4. THE DEFINITION OF MOLECULAR AND CRYSTAL STRUCTURES FOR EFFICIENT NONLINEAR PERFORMANCE

The definition of the basic molecular structure that can give rise to such effects opens the way for the synthetic chemist to develop empirically a range of suitable structures. There are of course a multitude of combinations of (donor–delocalized-system–acceptor) that can be synthesized. Experience of the relative donor and acceptor powers of various groupings coupled with the effectiveness of existing molecules allows some screening and makes it possible to target potentially efficient structures. Theoretical approaches can help to narrow the objectives and to develop novel systems.

(a) Theoretical prediction

Systematic computations can be carried out on larger molecules only by semiempirical techniques. The most successful of these has been based on the method of time-dependent perturbation theory, where the perturbed ground-state function is expanded in terms of the excited electronic states of the unperturbed molecule. The method, in this context, is often referred to as the sum-over-states (SOS) method (Pugh & Morley 1987). The formalism of the method sometimes leads to considerable confusion in qualitative statements and interpretation. In essence, the excited-state wave-functions are introduced only as a set of expansion functions, that when mixed with the original ground state give a description of the molecule as perturbed by the electric field of the radiation. The advantages of this procedure arise from the fact that the formulae for the polarizabilities contain some of the observable properties of the excited states, which can be replaced by their experimental values. The method can therefore be calibrated against spectroscopic transition energies, oscillator strengths and dipole moments, all of which are much more easily measured than the hyperpolarizabilities themselves. There is also a long history of successful correlation and prediction of such properties in semiempirical quantum chemistry.

A general formula for the second-order hyperpolarizability involves a sum over terms equivalent to that on the right-hand side of equation (4) and also involves cross terms in which interaction occurs between different excited states (n and m) via matrix elements $\langle n|r|m \rangle$.
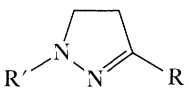
A computer program, CNDOVSB, based on a spectroscopic parametrization of the complete-neglect-of-differential-overlap (CNDO) method, suitable for polar conjugated molecules has been developed. The method is limited in the maximum size of the molecule that can be accommodated. At present only covalently bonded systems can be treated (Docherty et al. 1985; Pugh & Morley 1987).

The program has been used successfully to screen a large number of molecules for the magnitude of β. The reliability of this approach has been defined by the experimental confirmation of the predicted values using the electric field induced SHG technique (Levine 1977).

A notable novel prediction was the efficiency of the 2-pyrazoline grouping as the intermediate delocalized π-electron system in yielding molecules with high values of β.

TABLE 1. THE SECOND-ORDER HYPERPOLARIZABILITIES (β) OF 2-PYRAZOLINE AND RELATED MOLECULES (MORLEY & PUGH 1989)

(β_0 is the value calculated at $\omega = 0$ to avoid resonance effects, β_ω is the value for input wavelength $\omega = 1.06$ μm.)

R	R'	β_0	β_ω
—H	—H	1.7	2.9
—NH$_2$	—NO$_2$	28.6	137.6
—Ph	—Ph	18.5	100.5
—Ph·NO$_2$	—Ph·OMe	14	37
—Ph·OMe	—Ph·NO$_2$	60.3	624
—CH=C(CN)$_2$	—Ph	44.7	777.9

Table 1 shows the results obtained for a series of substitutions in the 1,3-positions. Of particular note is the manner in which the substitution of the 4-nitrophenyl and 4-methoxyphenyl groups is predicted to influence the value of β thus eliminating one arrangement from the synthetic programme. The last compound in the table; 3-(1,1-dicyanoethenyl)-phenyl-1,5-dihydro-1H-pyrazole (DCNP) has an exceptionally high value of β_ω. Following synthesis it was found to crystallize to form an acentric structure that is a potentially useful modulator (see below).
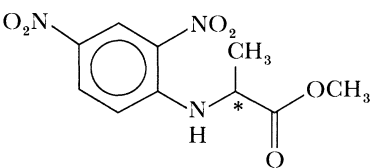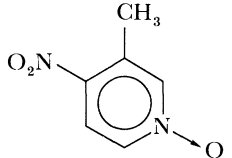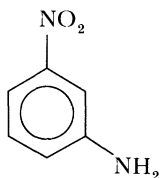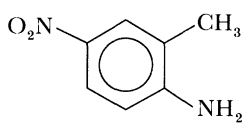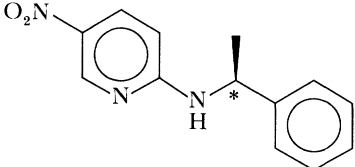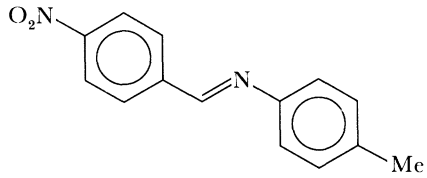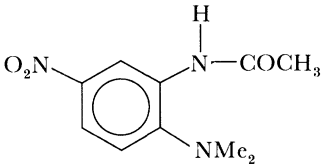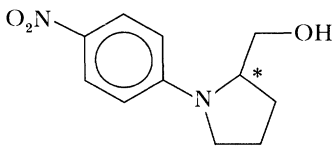
(b) *Formation of acentric structures*

The realization of the nonlinear optical properties of a solid comes from the arrangement of the molecules in the lattice to form an acentric structure. The probability of whether or not any organic molecule will crystallize in this way has been assessed by Nicoud & Twieg (1987). They conclude 'that organics have a much greater tendency to crystallize in space groups useful for SHG than their inorganic counterparts'. Despite this, the fraction of non-chiral organic molecules that do so is small (*ca.* 10%) and change cannot be relied upon. The reason for this low fraction is that strongly polar molecules tend to crystallize in parallel (centric) rather than collinear (acentric) 'head-to-tail' configurations.

One direct solution to this problem is to incorporate a chiral centre into the molecule. This automatically confers an acentricity on the molecule and defines that the solid will crystallize in one of the chiral, acentric space groups. Alternatively, a molecular engineering approach must be used whereby the shape and hence molecular packing characteristics are altered in an effort to reconfigure the molecule into an acentric structure.

The simplest example of the second approach is the compound 4-nitroaniline, which exhibits a high molecular polarizability ($\beta = 35 \times 10^{-30}$ cm^5 Fr^{-1}†) and promises to yield a high value of χ_2. This short linear molecule crystallizes to form a centric structure, however, and $\chi_2 = 0$. Simple substitution of the aromatic ring to form 2-methyl-4-nitroaniline ($\beta = 42 \times 10^{-30}$ cm^5 Fr^{-1}) causes the necessary adjustment in packing to yield an acentric structure with a high χ_2 (540 pm V^{-1}) and good nonlinear characteristics. An additional approach to encourage 'end-to-end' acentric packing has been to introduce a potential intermolecular

† 1 Fr ≡ 1 e.s.u. ≈ 3×10^{-10} C.

TABLE 2. ORGANIC MOLECULES WITH LARGE SECOND-ORDER NONLINEARITIES

molecule	substance (acronym)	powder SHG efficiency (urea = 1)
	2,4-dinitrophenyl-L-alaninemethylester (MAP)	10
	3-methyl-4-nitropyridine-N-oxide (POM)	14
	3-nitroaniline (mNA)	40
	2-methyl-4-nitroaniline (MNA)	80
	(−)2-(α-methylbenzylamino)-5-nitropyridine (MBANP)	81
	4-nitro-4′-methyl(benzylidineaniline) (NMBA)	104
	4-(N,N-dimethyl-amino)-3-acetamidonitrobenzene (DAN)	115
	N-(4-nitrophenyl)-(L)-prolinol (NPP)	150

hydrogen bonding system into opposite ends of the molecule. Both approaches have been combined to considerable effect by Zyss *et al.* (1984) in the well-designed molecule NPP (table 2), which is one of the most efficient nonlinear optical molecules available.

While conferring acentricity on the system such 'engineering' can have unfortunate side-effects such as decreasing the hyperpolarizability relative to that of the basic unit or altering the transparency range (Nicoud & Twieg 1987). Despite these minor problems, however, the application of these principles has resulted in the development of a wide range of potentially useful molecules. Some examples of these which are being studied at the present time are given in table 2 where they are ranked in order of powder SHG efficiency (Kurtz & Perry 1968).

These molecules show severally all of the solutions to defining acentricity noted above. The presence of side groups to direct the structure (MNA, DAN) into an acentric form, chiral centres (MBA-NP, MAP, NPP) and the development of intermolecular hydrogen bonding to encourage head-to-tail crystallization (NPP).

(c) *Optimization of molecular structure*

This attainment of a molecule of high hyperpolarizability in an acentric structure is not in itself sufficient to yield ideally efficient performance. For this the structure must be optimized to suit the property under development.

To maximize the linear electro-optic (Pockels) effect it is necessary to develop the highest polarization attainable in the sample. This is best achieved in a structural arrangement in which the molecular dipoles are aligned. This type of configuration is achieved in both MNA (Lipscomb *et al.* 1981) and DCNP (Allen *et al.* 1988). Both molecules show excellent linear electro-optic effects with reduced half-wave voltages of, respectively, $V_\pi = 1.3$ kV and $V_\pi = 370$ V compared with $V_\pi = 3.5$ kV for lithium niobate.

Such structures are inefficient, however, for parametric applications as SHG when for maximum efficiency the incident and doubled light must be phase matched. This requires that the ordinary refractive index at one of the frequencies should be matched with the extraordinary index at the other. This means that effects in two orthogonal directions are involved. When all the nonlinear effect is along one axis phase matching is not possible.

Zyss & Oudar (1982) have calculated the optimum orientations of the molecular dipoles in the solid to achieve the most efficient coupling in a range of structures. For the $P2_1$ structure the optimum angle is $\theta_m = 58.740°$ to the symmetry axis. The variation of efficiency with dipole angular orientation is well demonstrated by the materials given in table 3.

It should be reiterated at this point that these two outstanding materials were specifically designed to produce the effects noted.

TABLE 3. INFLUENCE OF THE RELATIVE ORIENTATION OF THE MOLECULES IN THE ACENTRIC LATTICE ON THE EFFICIENCY OF PHASE MATCHING (NICOUD & TWEIG 1987)

material	space group	θ^a/deg	θ_m/deg	powder SHG efficiency (urea = 1)
NMDA[b]	$P2_1$	89.9	58.7	1
DAN	$P2_1$	70.8	58.7	115
NPP	$P2_1$	58.6	58.7	150

[a] θ is the angle between the molecular dipole and the b-axis of the structure.
[b] NMDA: 4-nitro-dimethylaniline.

DCNP was designed theoretically by Morley & Pugh (1989) and defined in this way to have an extremely high dipole moment. Subsequent synthesis and crystallization yielded a highly acentric form of ideal structure and hence further molecular engineering was not necessary.

NPP was designed by Zyss *et al.* (1984) to conform to a molecule of high β with end groups arranged to yield intermolecular hydrogen bonding and hence to secure the head to tail configuration. The shape of the molecules defined the ideal optimum structural arrangement.

Both molecules represent a triumph of the combination of theory and empiricism applied to this problem.

5. DEVELOPMENT OF ORGANIC CRYSTALS FOR NONLINEAR OPTICS

The complete evaluation, definition and, in some cases use of the nonlinear properties of these materials requires that they can be prepared in the form of highly perfect single crystals. In general terms the preparation of organic crystals is a well-defined art. A wide range of types of crystal have been prepared by using adaptations of the basic techniques for the crystallization of solids from the melt, vapour phase or solution (McArdle & Sherwood 1987; Hooper *et al.* 1985). Very little particular attention had been paid to the crystallization of highly polar organic materials before Badan *et al.* (1987) described the preparation of several materials including POM, NPP and MAP. There remains a need to characterize the growth process to define how improved samples of a greater range of crystals can be prepared.

(a) Purification

A necessary prerequisite for success in crystal growth is the availability of highly pure starting material. The large-scale synthetic methods used to prepare organic solids yield products of not more than 99 % purity. Using developments in standard procedures (recrystallization, chromatography and gradient sublimation adapted to large-scale use (50–100 g)) coupled with the various forms of zone-refining (vapour, melt and travelling solvent) allow this to be improved to as high as 99.999 % purity in favourable cases (McArdle & Sherwood 1985).

The range of these procedures that can be applied to the present solids is limited by their properties: instability on melting or sublimation, solvate formation in solutions, etc. Despite this, however, purities in the range 99.99–99.995 % have been achieved for materials such as MAP, NPP and POM (Badan *et al.* 1987) and urea, NMBA, MBA-NP, DAN and DCNP (J. N. Sherwood and co-workers, unpublished work).

This level of purity has proved to be adequate for crystal growth.

(b) Bulk crystal growth

The principal objective in the crystal growth of these materials is to produce crystals of large size (10–100 cm³) from which can be cut and oriented specimens for the adequate evaluation of the nonlinear optical properties.

The crystal should be as free as possible from strain and crystal imperfections.

To achieve this one is limited to growth from the melt or from solution. The growth of organic crystals from the vapour phase is a slow process that often yields small crystals. Also, because growth takes place on a substrate there is inevitably a gradient of strain in the sample (McArdle & Sherwood 1987).
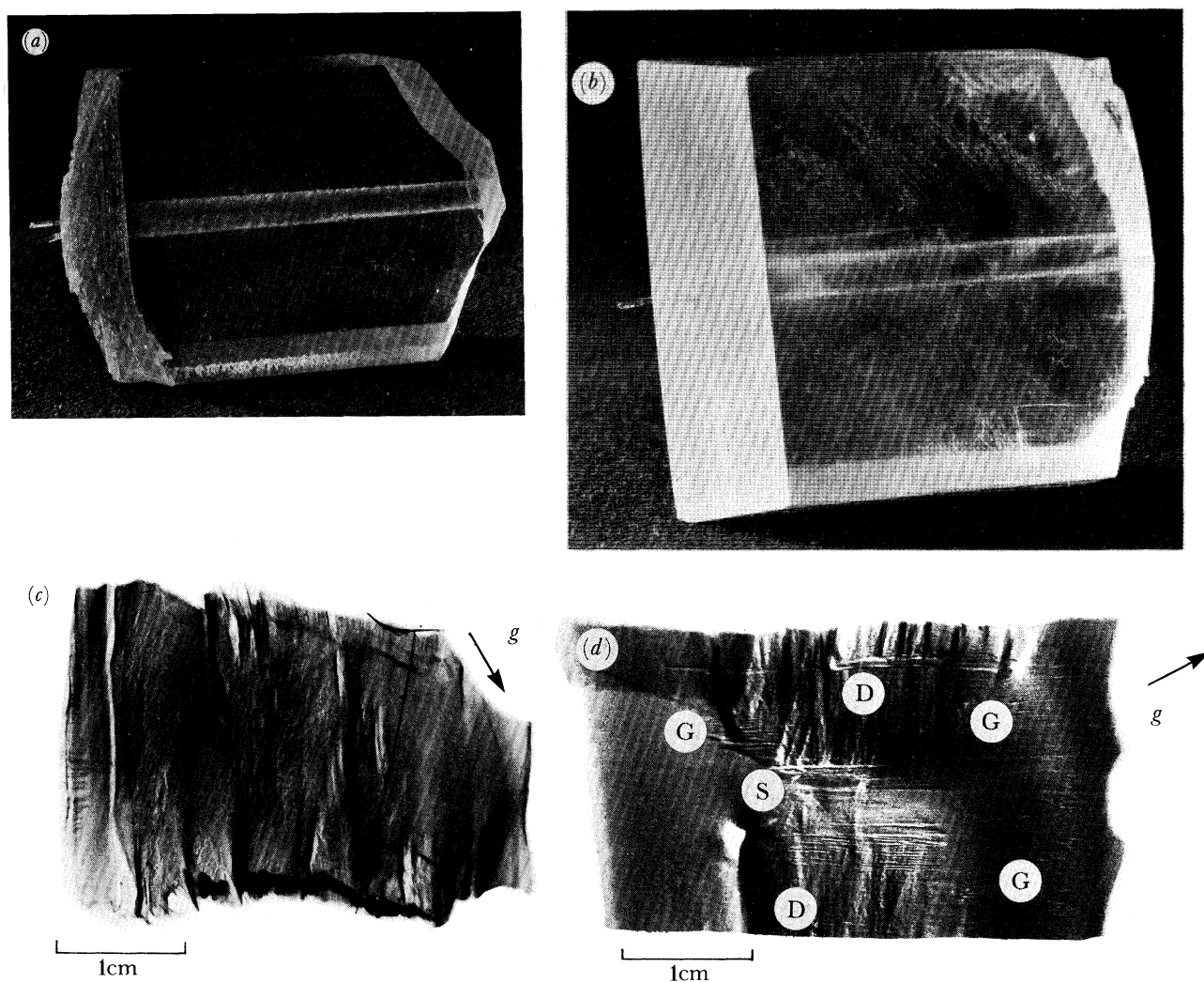
FIGURE 1. (*a*) Crystal of MBA-NP grown under conditions of medium supersaturation showing the roughening which develops on the [010] surfaces. The large surface is [001]. (Scale mark 1 cm.) (*b*) Facetted crystal of MBA-NP grown under conditions of lower supersaturation. (Scale mark 1 cm.) (*c*) Synchrotron radiation topograph of an (010) section of the specimen shown in (*a*). The distortion in the image arises from strain variations that develop in the crystal during growth. (Scale mark 1 cm.) (*d*) Synchrotron radiation topograph of an (010) section of a high quality specimen of MBA-NP. The seed S can be seen at the centre of the image; from this dislocation bundles D and growth sector boundaries G radiate to (respectively) the {001} surfaces and the intersection of the faces. (Scale mark 1 cm.)

Growth from solution under near equilibrium conditions offers the best prospect of yielding large crystals of high perfection and free from thermal strain in periods of 2–3 weeks.

The alternative method, growth from the melt by the Bridgman technique, involves controlled solidification in a closed vessel under extreme temperature gradients. This can generate strain in the crystal. There is also the problem of melt stability. Against these problems we can set the advantage that the extreme temperature gradients used provide high supersaturation and hence samples can be produced in short growth times (1–2 days), a valuable gain when the material decomposes slowly. Also, when the solid has suitable mechanical properties the crystals produced can be free from strain (McArdle & Sherwood 1987; Sherwood 1989).

The present materials have particular properties that present problems to the crystal grower. Their chemical complexity and nature often results in instability both in the solid at high temperatures (near to melting) and in the melt. The high polarity results in the ready formation of solvates both in solution and in the solid state. Polymorphism is common and its occurrence varies with solvent and crystallization conditions (Hall *et al.* 1986). It is imperative therefore to confirm that the required polymorphic form is produced under the conditions used for growth.

Additionally, the acentric forms of the more highly polar materials show extremes of growth behaviour, giving either rapid, uncontrolled and imperfect growth or zero growth along the polar direction. This problem can arise for the same material in different solvents or under different conditions of supersaturation. The inability to control this can have an adverse effect on the perfection of the product. The development of POM by Zyss and his co-workers (Hierle *et al.* 1984) represents an attempt designed to overcome this problem. POM has a zero dipole moment in the ground state and hence shows good growth characteristics that allow the preparation of prismatic crystals from solution. POM is, however, rather a unique case and the preparation of higher performance, more polar materials requires more careful handling.

The particular problems and how they may be overcome can be illustrated by a brief description of the preparation of MBA-NP.

(i) *MBA-NP*

This material is unstable in the melt and in the solid state at high temperatures. Solution growth offers the best means for crystal production. The primary step in solution growth is the identification of a suitable solvent. By trial and error, methanol was identified as the best solvent having a moderate solubility for MBA-NP (250 g kg^{-1} at 300 K) and yielding seed crystals of a prismatic habit. Development of these seeds in a standard solution growth system (Hooper *et al.* 1985) resulted in the problems referred to above. Under high supersaturation conditions the seeds showed rapid growth in one [010] (polar) direction. Reduction in the supersaturation led to improved growth but the crystals still showed very rough interfaces in this direction (figure 1*a*, plate 1). A final adjustment of growth conditions allowed the facetting of the [010] interfaces and the production of optically perfect crystals (figure 1*b*, plate 1) (Morrison *et al.* 1990).

It will be noted from the plate that both samples show a high degree of optical clarity. Despite this apparent perfection, growth under non- or rough-facetted conditions results in the development of strain in the samples. This is demonstrated by the two synchrotron X-ray topographs shown as figure 1*c, d*, plate 1. The former, taken using a section from a crystal of

equivalent quality to that shown in figure 1 a is indicative of a high degree of deformation in the sample. The latter, from a high-quality specimen, shows the more expected result in which can be discerned the seed (S) at the centre and dislocations (D) and growth-sector boundaries (G) diverging from this to the faces and corners of the crystal. Even in this specimen, however, there is an overall dark contrast indicative of residual strain in the crystal. It has not yet proved possible to overcome this.

Samples of this quality are readily oriented, cut and polished to yield samples of good optical quality (parallelism 30 sec arc, flatness $\frac{1}{10}\lambda$, scratch width 0.5 μm) without the introduction of further imperfections.

The intensity of SHG depends markedly on the structural perfection of the solid. By using a cut and polished section of the crystal the topograph of which is shown in figure 1 d, it was possible to map the relative efficiency of SHG in regions of difficult perfection. All regions of the crystal other than in the close vicinity of the seed were optically transparent and allowed transmission of the laser beam with no apparent distortion. Figure 2 shows a comparison between the phase-matched peaks obtained from the best and worst regions. The maximum intensity differs by a factor of 3. This confirms the need for high quality to achieve ultimate performance.
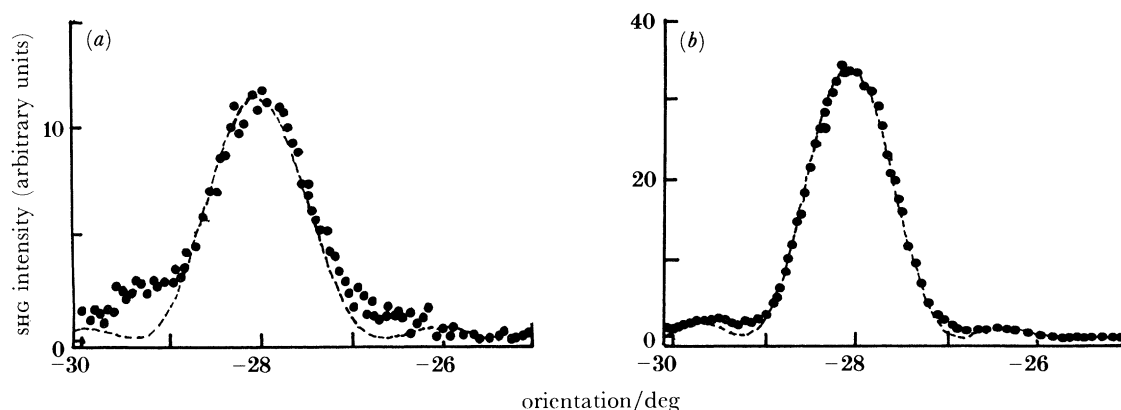

FIGURE 2. The coincidence between the observed and calculated variation in SHG intensity for MBA-NP. (a) Imperfect (dislocated) region; (001) sector of figure 1 d. Incident plane (010), orientation around the [100]-axis. The dotted curve represents the theoretically expected variation. (b) Perfect region; lateral sectors of figure 1 d.

A parallel variation has been noted for the laser damage threshold but not yet quantified; the less perfect samples showing a lower damage threshold (see below).

6. Optical properties

By using crystals developed as described the second-order nonlinear optical properties of a range of organic materials have been assessed. A selection of these properties – the largest components of the d-tensors that contribute to χ_2 and electro-optic coefficients (r) – are given in tables 4 and 5. Comparison with similar data for 'state of the art' inorganic materials show that they have considerable potential for complementary use as device materials and at much lower input power densities. Of equal importance to optical performance is the capability of the material to withstand high-power incident laser damage. This capability is as yet inadequately

TABLE 4. MATERIALS THAT SHOW EFFICIENT PHASE-MATCHED SHG

(n is refractive index; KTP is potassium titanyl phosphate; BBO is β-barium borate.)

material	phase-matching type	$d/(\text{pm V}^{-1})$	$d^2 n^{-3}/(\text{pm})^2 \text{ V}^{-2}$
organic			
urea[a]	I and II	$d_{36} = 2.3$	1.6
MBA-NP[b]	I	$d_{22} = 8.3$	13
POM[c]	I and II	$d = 10$	15
MAP[d]	I and II	$d_{22} = 18.4$	42
NMBA[e]	II	$d_{33} = 16.7$	53
DAN[f]	I and II	$d_{\text{eff}} = 27$	145
NPP[g]	I and II	$d_{21} = 84$	1210
inorganic			
KTP[h]		$d_{33} = 13.7$	32
BBO[i]		$d_{22} = 4.1$	2.9

[a] Halbout et al. (1979). [b] Bailey et al. (1988 a, b). [c] Zyss et al. (1981). [d] Oudar & Hierle (1977). [e] Bailey et al. (1989). [f] Baumert et al. (1989). [g] Ledoux et al. (1986). [h] Driscoll et al. (1986). [i] Kato (1986).

TABLE 5. PRINCIPAL ELECTRO-OPTIC COEFFICIENTS (r) AND REDUCED HALF-WAVE VOLTAGES (V_π) FOR ORGANIC AND INORGANIC MATERIALS

material	$r/(\text{pm V}^{-1})$	V_π/V
organic		
urea[a]	$r_{41} = 1.9$	—
POM[b]	$r_{52} = 5.1$	—
mNA[c]	$r_{33} = 16.7$	—
MNA[d]	$r_{12} = 67$	1300
DCNP[e]	$r_{33} = 160$	370
inorganic		
LiNbO$_3$[f]	$r_{33} = 30.1$	3500
KDP[f]	$r_{63} = 26.4$	9300

[a] Morrell et al. (1979). [b] Sigelle & Hierle (1981). [c] Stevenson (1973). [d] Lipscomb et al. (1981). [e] Allen et al. (1988). [f] Kaminova & Turner (1971).

defined by comprehensive examinations, but it does seem that these materials may well show their original promise. Very high laser damage thresholds have been reported for crystals of some materials which represent factors of 10–100 times improvement over many inorganic systems (POM: more than 270 MW cm^{-2} 7 ps pulsed YAG, 50 MW cm^{-2} 15 ns pulsed YAG; (Zyss et al. (1985); (MBA-NP: 120–500 MW cm^{-2}, 15 ns pulsed YAG; (J. N. Sherwood, unpublished work)). There is no doubt that the lower values in the range for MBA-NP can be associated with lattice imperfection and surface damage. This implies that more perfectly prepared materials could more regularly yield damage thresholds at the upper end of the range. This still remains to be confirmed.

The major current restriction to the wide use of organic materials is the limited range of their applicability. For parametric applications only urea operates well in the ultraviolet–visible range and crystals for frequency doubling and optical parametric oscillation are commercially available. The remaining materials are transparent at much longer wavelengths (greater than 500 μm). This range includes the frequencies of operation of lasers which are likely to be used in telecommunication systems. A similar limitation holds for the potential electro-optic modulation materials. However, even though the absorption edges of MNA (460 nm, Levine

et al. 1979) and DCNP (570 nm, Allen *et al.* 1988) limit their range of applicability their performance is excellent.

The future challenge is therefore not only to develop more efficient materials, but to spread the range of applicability to shorter wavelengths. The molecular design capabilities have been proved. There is no reason why novel materials should not be developed that would allow the efficient 'doubling' and mixing of radiation to access the 'blue end' of the spectrum.

To bring this to fruition requires the continued combination of expertise which has been applied successfully to this problem to date. With the collaboration of synthetic and theoretical chemists to target novel materials, materials scientists to define the essential structural aspects of crystallography and crystal growth and physicists and electrical engineers to evaluate and use the optical properties, then these materials have a high prospect of finding use as commercial devices.

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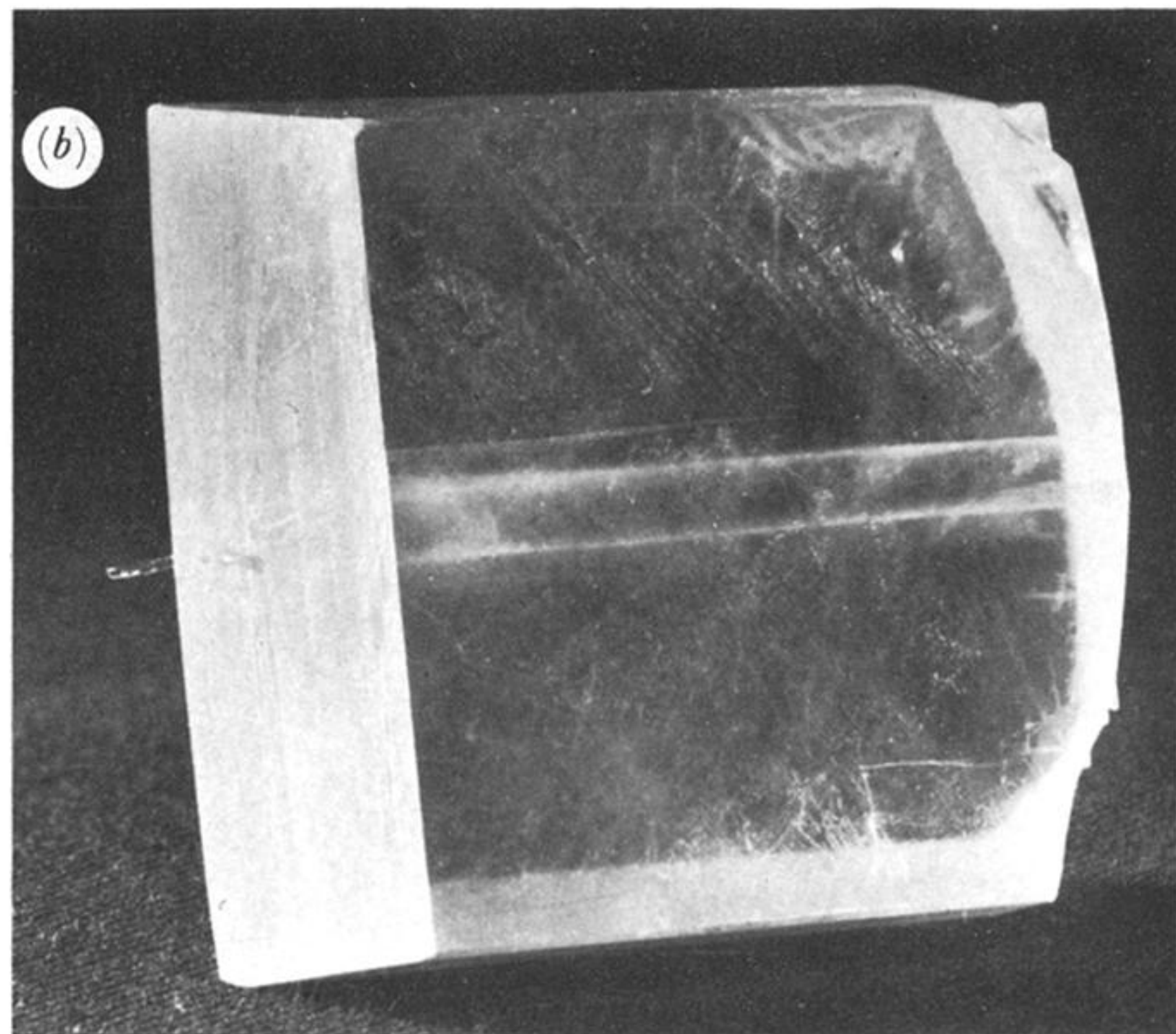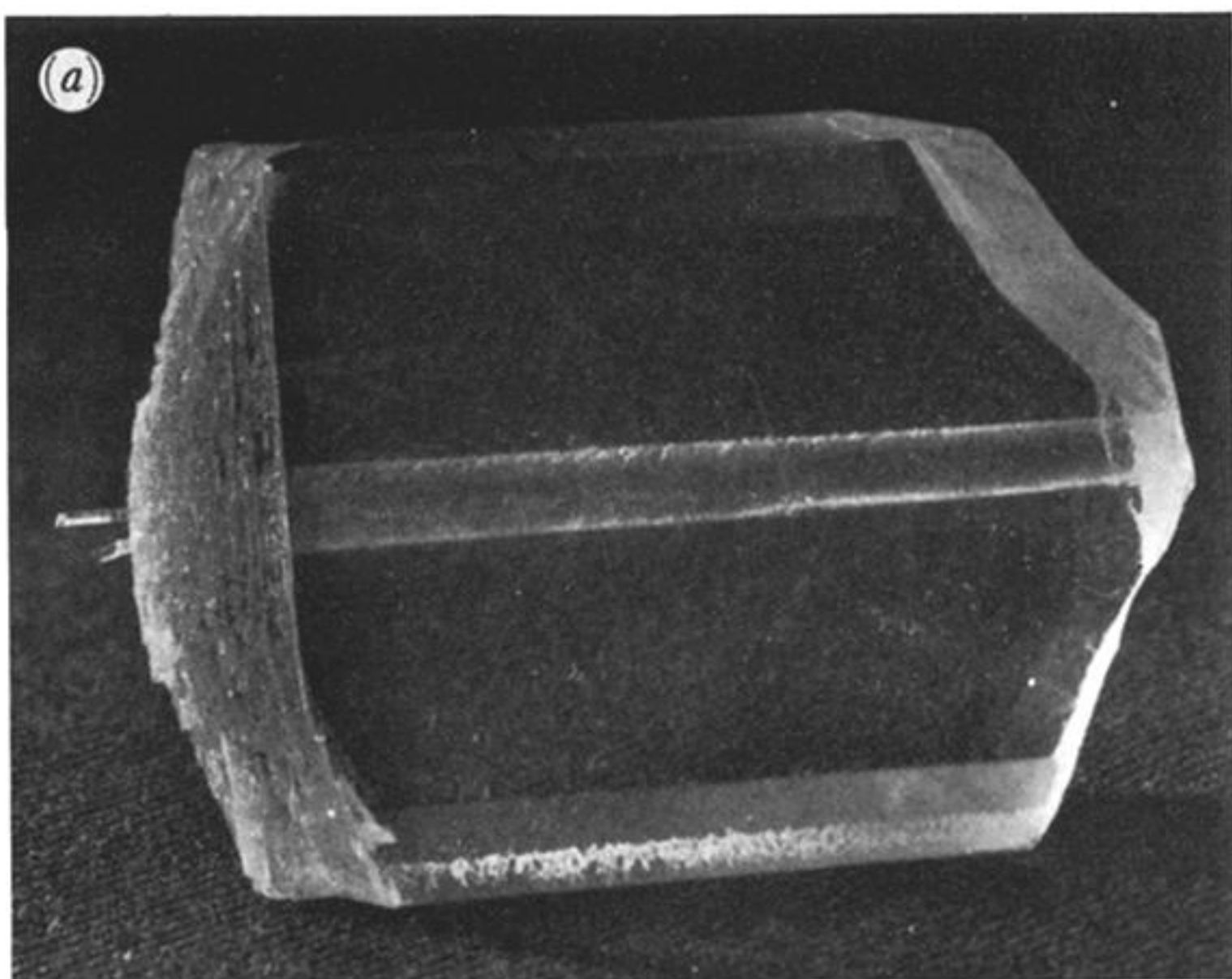Zyss, J. & Oudar, J. L. 1982 *Phys. Rev.* A **26**, 2028–2048.

Discussion

H. J. COLES (*Liquid Crystal Group, Physics Department, The University, Manchester, U.K.*). In the generation of χ^2 nonlinear optical effects several physical phenomena such as phase matching of the incoming and second harmonic signals and the influence of resonant absorption of the frequency-doubled signals have to be considered. Many of the compounds Professor Sherwood describes with enhanced β values have a yellow appearance implying absorption in the blue–green spectral region. Because the pump laser light should ideally be in the near infrared (perhaps using laser diodes with a wavelength of the order of 850 nm), then the second harmonic signal will propagate at $\lambda \approx 425$ nm. This must pose problems for the realization of practical devices and raises a number of questions. Firstly, can the resonant and non-resonant contributions to β be differentiated? Secondly, what chemistry can be imagined that would head to high β values without absorption of the second harmonic signal? Thirdly, in the data for β and χ^2 can he comment on what excitation wavelength were used in the measurements or calculations?

J. N. SHERWOOD. The lowest-energy electronic absorption bands in most of the compounds described here are in the range 300–400 nm. There should be no major reabsorption of the second harmonic if the fundamental wavelength is above 850 nm. There may, of course, be problems relating to absorption of the second harmonic at defects, impurities or through multiphoton processes.

Most experiments have been carried out with 1.06 μm YAG fundamental. Frequency shifted YAG at 1.3, 1.5 or 1.9 μm is used for larger conjugated systems.

At shorter wavelengths there will evidently be problems with extended polar aromatic structures. Large transfer of electronic charge on excitation can be obtained in other systems, typically donor–insulator–acceptor arrangements, where groups having high-energy electrons in energetically different states are separated by a saturated linkage. These still remain to be investigated.

Although pre-resonant enhancement is important in maximizing the effect, there is always a substantial non-resonant effect still present at very low frequencies in the type of molecule described. The pre-resonant and non-resonant effects have the same origin – in the π-electron system – and the latter cannot therefore exist in the absence of the low-energy $\pi \to \pi^*$ transitions. For example, pNA in dioxan has its charge transfer $\pi \to \pi^*$ transition at 365 nm. Electric-field-induced SHG (EFISH) values of β_x are respectively 16.9 and 40 Fr cm^5 at 1.064 µm and 830 nm. Extrapolation of frequency-dependent measurements and theoretical work lead to a value of about 8 Fr cm^5 at very low frequencies.
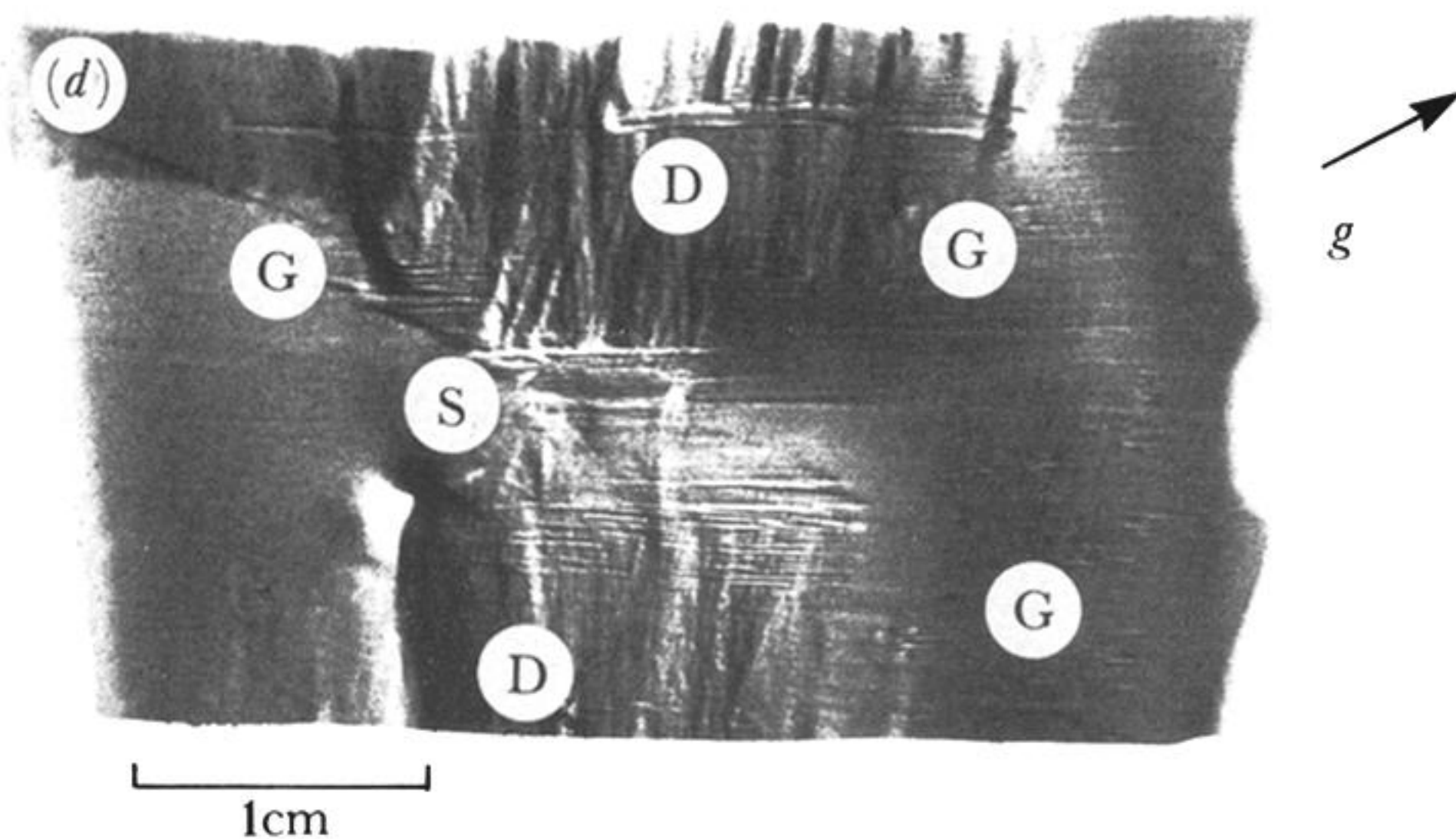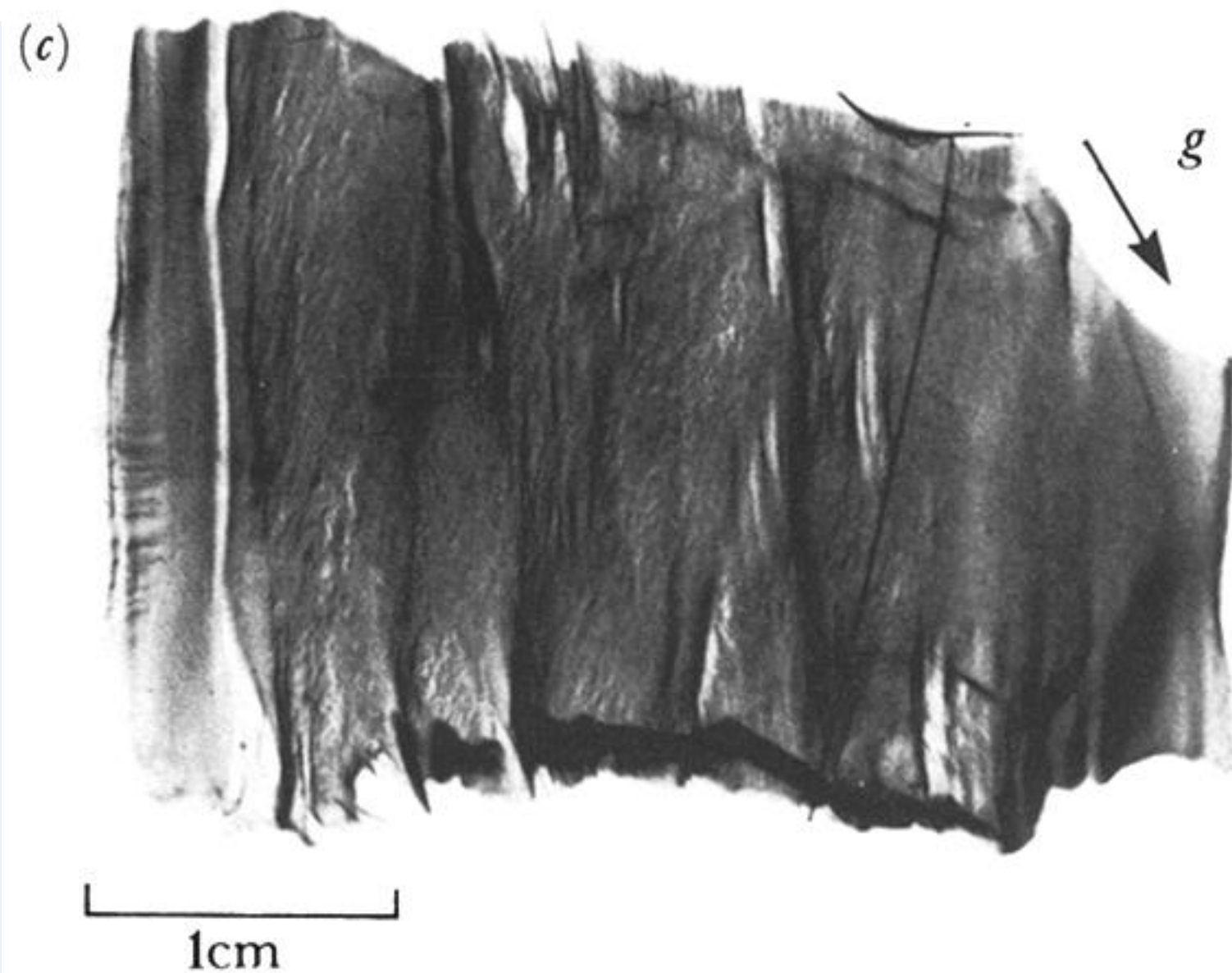
FIGURE 1. (a) Crystal of MBA-NP grown under conditions of medium supersaturation showing the roughening which develops on the [010] surfaces. The large surface is [001]. (Scale mark 1 cm.) (b) Facetted crystal of MBA-NP grown under conditions of lower supersaturation. (Scale mark 1 cm.) (c) Synchrotron radiation topograph of an (010) section of the specimen shown in (a). The distortion in the image arises from strain variations that develop in the crystal during growth. (Scale mark 1 cm.) (d) Synchrotron radiation topograph of an (010) section of a high quality specimen of MBA-NP. The seed S can be seen at the centre of the image; from this dislocation bundles D and growth sector boundaries G radiate to (respectively) the {001} surfaces and the intersection of the faces. (Scale mark 1 cm.)