of a constant mass [1]. In the present case the change of mass due to evaporation of the sample necessitated a discontinuous method of obtaining data which is less accurate, and so a mechanistic interpretation of the n value is not possible. However, the activation energy of $231 \pm 5.0\,\text{kJ mol}^{-1}$ obtained in the present work is close to $260\,\text{kJ mol}^{-1}$ for diffusion of Cl^- in NaCl [10] and suggests that volume diffusion is the mechanism of mass transport during sintering NaCl. When CdCl_2 is dissolved in NaCl the Cd^{2+} on an Na^+ site is effectively an extra charge on the site, i.e. Cd^+. For charge neutrality in the crystal we then have

$$[\text{Cd}^+] + [V_{\text{Cl}}^+] = [V_{\text{Na}}^-]$$

where $[V_{\text{Cl}}^+]$ and $[V_{\text{Na}}^-]$ are the concentrations of charged anion and cation vacancies respectively, and an increase in Cd^+ will disturb the mass-action equilibria of anion and cation vacancies. The effect of adding CdCl_2 to NaCl is to decrease the concentration of vacancies for diffusion of the rate-controlling Cl^-. On this basis, the decrease in sintering rate on addition of CdCl_2 to NaCl (Table I) is due to a decrease in the rate of volume diffusion. Morgan *et al.* [5] interpreted a kink on the shrinkage–temperature curve of pure NaCl and NaCl containing 0.1 mol % CsNO_3 as possibly due to the interaction of the impurity atoms with dislocations, and further assumed that possible plastic flow was the cause of densification. The temperature dependence of volume diffusion and high temperature plastic flow would be similar since the plastic flow would involve either diffusional creep and/or some diffusion process whereby dislocation climb would permit movement of jogged or otherwise immobile dislocations. If the rate-controlling process is plastic flow, the role of the dissolved Cd^{2+} would be hinder the motion of dislocations. In duscussion the precipitation hardening and dislocation locking in NaCl containing CdCl_2, Newey *et al.* [11] suggested that the most likely mechanisms of strengthening at high temperatures is the one that produces locking of stationary dislocations and imposes a drag on moving dislocations, and that impurity ion-generated vacancy dipoles are the effective locking agents. On the present results, both dislocation hardening and mass transport by volume diffusion appear equally possible as the transport process during sintering pure and CdCl_2–doped NaCl.

References

1. F. THÜMMLER and W. THOMMA, *Met. Rev.* **12** (1967) 69.
2. W. D. KINGERY and M. BERG, *J. Appl. Phys.* **26** (1955) 1205.
3. J. B. MOSER and D. H. WHITMORE, *ibid* **31** (1960) 488.
4. R. L. COBLE and J. E. BURKE, in "Progress in Ceramic Science", Vol. 3, edited by J. E. BURKE (Pergamon Press, London, 1963) p. 219.
5. C. S. MORGAN, L. L. HALL and C. S. YUST, *J. Amer. Ceram. Soc.* **46** (1963) 599.
6. A. A. AMMER and D. W. BUDWORTH, *Proc. Brit. Ceram. Soc.* 3 (1965) 185.
7. P. W. CLARK and J. WHITE, *Trans. Brit. Ceram. Soc.* 49 (1950) 305.
8. S. T. RASMUSSEN and I. V. CUTLER, *Trans. J. Brit. Ceram. Soc.* **71** (1972) 5.
9. J. H. ROSOLOWSKI and C. GRESKOVICH, *J. Amer. Ceram. Soc.* **58 (1975) 177.**
10. W. D. KINGERY, in "Introduction to Ceramics" (Wiley, New York, 1960) p. 229.
11. C. W. A. NEWEY, R. P. HARRISON and P. L. PRATT, *Proc. Brit. Ceram. Soc.* 6 (1966) 305.

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Second harmonic generation in organic crystals

Current interest in optical communication systems has stimulated the investigation of new, effective materials for electro-optic modulation. In most instances, the work has been restricted to inorganic materials of comparitivelv complex composition, e.g. lithium niobate, potassium tantalate niobate, barium sodium niobate. Severe problems have been encountered with the preparation of optically homogeneous specimens of these materials, usually because the concentrations of the individual elements are a function of growth rate, temperature, undercooling etc. Striation-free crystals are seldom available, even on a research scale. Furthermore, materials of this type generally have high dielectric constants which reduce their effectiveness as high frequency modulators. Although several elegant procedures have been suggested for pulling striation-free crystals [1], only the relatively simple materials, lithium niobate and lithium tantalate, are currently available commercially.

The use of organic materials for electro-optic applications has been proposed [2] and a practical form for a "filled fibre" modulator has been described by Stevenson and Dyott [3]. However, very few materials have been studied for this purpose yet potentially there are innummerable organic substances to choose from.

The advantages of organic materials are: (1) they are generally cheap to synthesize; (2) they can be conveniently purified by conventional techniques; (3) they have low dielectric constants; (4) provided that the crystals are pure, they will be striation free since compositional variations cannot occur.

The main problem encountered in the search for "new" electro-optic organic crystals is the method employed for detecting and quantifying the effect. Clearly it is too time-consuming to purify, grow crystals, determine the structure, fabricate and test specimens of each material. Preferably, a simple procedure is desirable that will allow many materials, obtainable as small crystallites, to be tested. The present note deals with this aspect of the search for "new" materials.

The 32 crystal classes may be divided into two sections, 11 with centrosymmetric and 21 with non-centrosymmetric point groups. The electro-optic effect can only occur in the latter group. A survey of known crystal structures by Rez [4] showed that non-centrosymmetric point groups occurred in about 42% of organic compounds as compared with 17% of inorganics.

Apart from the electro-optic effect, other important properties peculiar to non-centrosymmetric crystal structures are piezoelectricity and second harmonic generation (SHG). In these properties we have two methods of detecting potential electro-optic effects in organic crystals. The method of Giebe and Scheiber [5] has been used to detect piezoelectricity in microcrystalline samples and, more recently, a test for second harmonic generation was developed by Kurtz and Perry [6]. The latter method has been used by a number of other workers, e.g. Bass *et al.* [7], Jerphagnon [8], Southgate and Hall [9], Davydov *et al.* [10] and Bolognesi *et al.* [11] with particular reference to organic compounds.

Bloembergen [12] has shown that both the linear electro-optic effect and second harmonic generation may be described by non-linear susceptibilities. These susceptibilites are subject to a dispersion law similar to that governing the linear susceptibility, the latter becoming large in the region of an absorption band. Thus the electro-optic effect increases as the observation wavelength approaches an absorption edge and the SHG efficiency also increases as the exciting or emitted wavelength becomes absorbed. Therefore, the compounds selected for testing in this work were mostly coloured red or yellow so that an absorption band in the ultraviolet was sufficiently close to enhance both the elctro-optic effect at 0.6328 μm and SHG from 1.06 μm, but sufficiently distant not to adversely affect optical transmission at 0.6328 μm.

The electro-optic properties of the deep orange crystal 3-nitroaniline (mNA) have been extensively studied by Stevenson [13]. This compound, which showed the largest electro-optic coefficient yet determined for a non-ferroelectric crystal, was used here both as a starting point in a semi-logical selection of compounds for testing and as a comparative standard in the SHG tests.

To test for piezoelectricity, the compounds were first purified by zone refining, vacuum sublimation or crystallization from solution in organic solvents. A Wayne–Kerr resonance bridge was used to supply an alternating voltage of variable frequency to a sample cell containing small crystals held between two flat electrodes. Any piezoelectric resonances were detected by a coupled variably tuned circuit and amplified to give an audio signal.

This method of testing was only partially successful. The detectivity of the apparatus was sensitively dependent on the sizes and shapes of the crystals and the responses were generally small, e.g. mNA samples had to contain equant crystallites of the order 10 mm^3 in size before registering a positive result. From 60 compounds, only the four marked with an asterisk in Table I gave a positive result.

TABLE I

Material	Relative SHG efficiency
4-nitrophenylhydrazine (NPH)*†	1.6
3-nitroaniline (mNA)*‡	1.0
1-formyl 2-(4-nitrophenyl) hydrazine (FNPH)*	1.0
4-hydroxyazobenzene	0.8
acetophenone 4-nitrophenylhydrazone	0.8
4-nitrophenol	0.7
benzaldehyde 4-nitrophenylhydrazone	0.6
2-methyl 3-nitroaniline (2MmNA)*	0.5
1, 4-naphthoquinone	0.4
1, 3-dinitrobenzene‡	0.4
2, 4-dinitro 2′-methoxydiphenylamine	0.4
acenaphthene picrate	0.4
4-amino azobenzene	0.2
2, 4-dinitro 3′-methyldiphenylamine	< 0.2
N, N-dimethyl 4-nitroaniline‡	
3-nitrophenol‡	
3-aminophenol	
phthalodinitrile	
benzil‡	
potassium dihydrogen phosphate (KDP)	

* Positive piezoelectric signal given on Giebe-Scheibe testing

† Previously reported to be non-centrosymmetric [11].

‡ Found to be non-centrosymmetric by a survey of crystallographic literature (J. L. Stevenson, private communication).

To test for SHG, a sample of each compound was ground to an average particle size of about 100 μm and a layer of powder was stuck on to adhesive tape. The tape was placed below a dielectric mirror placed at 45° to the horizontal beam of a Q-switched Nd^{3+}/YAG laser so that the beam was deflected onto the powder. A pulsed beam of about 10 MW cm^{-2} was repetitively applied to each sample in turn; samples failing to generate green light visible to the naked eye were rejected at this stage. (A number of samples gave a white incandescence during the laser pulse. This was interpreted not as SHG but as an anti-Stokes effect.) Successful samples were re-prepared for use in a semi quantitative test. This test was begun at minimum laser power (about 0.5 MW cm^{-2}), and the power was slowly increased until green emission was just detectable. This laser pulse energy was measured with an E.G. + G. SGD 100 photodiode. The compounds are ordered in Table I with respect to "relative efficiency", i.e. the ratios of the threshold pulse energy required for SHG in mNA to that required for the respective samples. In the case of mNA, the threshold energy corresponded to an average beam power density of 1.6 MW cm^{-2}; however, the beam was not uniform so the real value was probably considerably higher since the first observed SHG was due to a "hot spot" in the beam.

Three of the compounds in Table I were examined with respect to their crystallography and crystal growth properties. These are discussed below.

4-nitrophenylhydrazine. Because of excessive decomposition in the liquid state at the melting point (182° C), crystals could not be grown from the melt. Growth from solution in ethanol or dioxan was also impaired by auto-oxidative decomposition. Small crystals could, however, be grown by vapour sublimation using nitrogen as a carrier gas at a pressure of 5 Torr and a temperature of about 150° C. Crystals obtained by this method were highly strained, but of sufficient quality to obtain Weissenberg photographs using Cu$K\alpha$ radiation.

The data obtained were:

a = 12.5 Å, systematic absences
b = 3.5 Å, $h0l(h = 2n + 1)$
c = 14.7 Å, $0kl(l = 2n + 1)$
Density 1.3 g cm^{-3}

Space group $Pca2_1$; $z = 4$.

1-formyl 2-(4-nitrophenly) hydrazine (FNPH). Good quality crystals of this compound were obtained by slow cooling of a solution in ethanol. Weissenberg photographs gave the following data.

$a = 10.3$ Å, systematic absences

$b = 9.5$ Å, $h0l(h = 2n + 1)$

$c = 8.0$ Å, $0kl(l = 2n + 1)$

Density $= 1.53\,\mathrm{g\,cm^{-3}}$

Space group $\mathrm{Pca2_1}$; $z = 4$.

2-methyl 3-nitroaniline (2MMNA). Although this compound did not decompose excessively at its melting point (89° C) zone refining was not effective for purification. Vacuum sublimation at 80° C using nitrogen at 5 Torr as a carrier gas purified the solid, and needle crystals up to 10 mm × 3 mm × 1 mm were obtained by this method. Some the the smaller crystal were used to obtain Weissenberg photographs:

$a = 14.4$ Å systematic absences

$b = 13.1$ Å $h00(h = 2\tfrac{1}{4}\,1)$

$c = 3.90$ Å $0k0(k = 2n + 1)$

Density $= 1.4\,\mathrm{g\,cm^{-3}}$

Space group $\mathrm{P2_12_12_1}$; $z = 4$.

An attractive feature of organic crystals for electro-optic modulation is the possibility of a predominantly electronic mechanism for the electro-optic effect [14] which can operate free from lattice vibrations and therefore can be dissociated from an piezoelectric effects. Clearly, a selection method based quantitively on piezoelelectricity would here be counterproductive. The above work has shown that the Giebe–Scheiber method, when applied to organic compounds, has a low detectivity. This result supports expectation that, in general, piezoelectric resonances are not as pronounced in organic crystals as in their inorganic counterparts (the mechanical Q of organic crystals is generally small). However, the compounds detected by this method were only about 20% of all the non-centrosymmetric solids discovered and are not necessarily the most suitable for modulator constructuon.

The SHG technique, on the other hand, is not affected by lattice vibrations which are spectrally far removed from the exciting radiation. The SHG efficiency is enchanced by the extent of electrical asymmetry and the intensity of optical transitions in a similar manner to the electro-optic effect. Therefore, the relative SHG efficiencies of powders are a semiquantitative guide to the electro-optic properties of the crystals. (Deviations from an exact correlation between the two effects are caused by dispersion and the critical phase matching conditions required for SHG.)

The approach taken in this study differed from previous works in three respects. The preliminary selection of compounds was based mainly on their absorption spectra, i.e. compounds with a deep yellow or red colour were chosen. The semiquantitive comparison of the compounds was simplified by the omission of an electronic detection system. Lastly, consideration was given to a further selection rule which must apply, i.e. the feasibility of crystal growth.

Of the compounds showing better that average SHG, three were chosen for preliminary crystallographic study. 4-nitrophynylhydrazine gave the best SHG result and its crystal habit and dichroism indicated a favourably strong anisotropy. However, it was considered that the crystal growth of this compound would present formidable problems. 2-methyl 3-nitroaniline gave less pronounced SHG but its electro-optic behaviour is worthy of further study as it would provide a useful comparison with its analogue, 3-nitroaniline, which has been treated theoretically as well as experimentally [15]. 1-formyl 2-(4-nitropheny) hydrazine showed SHG comparable to 3-nitroaniline and was selected for a more detailed investigation. A later paper will report the evaluation of its optical electro-optic properties.

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References

1. J. C. BRICE, "The Growth of Crystals from Liquid" (North-Holland, Amsterdam, 1973).
2. S. AYERS, M. M. FAKTOR and J. L. STEVENSON, *J. Mater. Sci.* 7 (1972) 31.

3. J. L. STEVENSON and R. B. DYOTT, *Electronics Letters* **10** (1974) 449.
4. I. S. REZ, *Soviet Phys. Crystallog.* **5** (1960) 63.
5. W. D. CADY, *Piezoelectricity, Dover (N.Y.)* **1** (1964) 231.
6. S. K. KURTZ and T. T. PERRY, *J. Appl. Phys.* **39** (1968) 3798.
7. M. BASS, D. BUA, R. MOZZI and R. R. MONCHAMP, *Appl. Phys. Letters* **15** (1969) 393.
8. J. JERPHAGNON, *I.E.E.E. J. Quant. Elect.* **QE7** (1971) 42.
9. P. D. SOUTHGATE and D. S. HALL, *J. Appl. Phys.* **43** (1972) 2765.
10. B. L. DAVYDOV, V. V. DUNINA, V. F. ZOLIN and L. G. KORENVA, *Optic. Spectrosc.* **34** (1973) 150.
11. G. P. BOLOGNESI, S. MEZZETI and F. PANDARESE, *Opt. Commun.* **8** (1973) 267.
12. N. BLOEMBERGEN, "Nonlinear Optics" (Benjamin, New York, 1965).
13. J. L. STEVENSON, *J. Phys. D.* **6** (1973) L13.
14. F. N. H. ROBINSON, *Bell System Tech. J.* **46** (1967) 913.
15. J. L. STEVENSON and A. C. SKAPSKI, *J. Phys. C.* **5** (1972) L233.

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On the influence of dislocations on the thermal migration of liquid inclusions

In a recent paper on the annealing of liquid lead inclusions in an aluminium lead alloy, McLean and Loveday [1] found that the inclusions migrated in the thermal gradient, produced by the electron beam, in the hot stage of a high voltage electron microscope. Those inclusions that were larger than 0.8 μm radius migrated at a velocity independent of the droplet size, the expected result for diffusion-controlled thermal migration [2]. However, droplets smaller than 0.8 μm migrated more slowly, apparently indicating some measure of interface inhibition of the thermal migration [2], and droplets smaller than 0.1 μm did not appear to move at all. This is an extremely surprising result as the weight of experimental and theoretical evidence suggests that the solid–liquid interface in metals and other low entropy of melting materials is extremely mobile (e.g. [3–6]).

There are two models of the solid–liquid interface migration, the one used by McLean and Loveday [1] following, for example, Tiller [7], for kinetically faceted interfaces which requires an emerging screw dislocation to provide a spiral ledge at which solidification (for liquid inclusions, melting [8]) can occur. This leads to a relationship between the interface velocity, v_i, and the interface undercooling (or superheating), ΔT_i, given in Equation 1, where μ_2 is the appropriate mobility.

$$v_i = \mu_2 \Delta T_i^2 \qquad (1)$$

If the interface is atomically rough as expected for metals [6], then much faster interface kinetics are expected with

$$v_i = \mu_1 \Delta T_i \qquad (2)$$

McLean and Loveday reported initially a value of μ_2 that was 0.09 mm sec^{-1} K^{-2} but following a correction of a mistake in their paper [1a] that changed the observed value of the temperature gradient from 1.85×10^4 K m^{-1} to 1.85×10^5 K m^{-1}, the value of μ_2 fell by a factor of 100. This new value of μ_2 is unacceptable both theoretically and, more significantly, experimentally, since it would indicate the need for undercoolings for aluminium solidification that are much larger than the vanishingly small values found in practice [3–6], a result recently confirmed yet again in aluminium by Burden and Hunt [9]. Burden and Hunt reported that they could find no measurable undercooling (less than 0.1 K) for an aluminium casting that froze at something like 0.5 mm sec^{-1} *, which if μ_2 was either 0.09 or 9×10^{-4} mm sec^{-1} K^{-2} would need undercoolings of 2.3 or 23 K respectively.

If McLean and Loveday's results are re-analysed

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*This velocity was estimated from the ratio of latent heat of fusion to the liquid specific heat of aluminium (365 K) and from the observation that the liquid cooling rate was 625 K min^{-1} so the freezing time will be about 365/625 min (35 sec) for a casting of 17 mm radius.