

Second-harmonic generation by composite materials

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A characteristic of non-centrosymmetric crystal structures is the ability to generate the second harmonic from intense light beams. The magnitude of the effect is dependent on the square of the input intensity. Thus, emission from a Nd-YAG laser at a wavelength of $1.06\ \mu\text{m}$ is partly converted to green light at $532\ \text{nm}$. For practical applications in spectroscopy, inorganic single crystals are used as frequency doublers. Recently, there has been much interest in frequency doubling by organic compounds and by polymers because the relevant non-linear optical coefficients can be very much higher and thus there is the possibility of operation at much lower light intensities [1, 2]. Such materials might be used as single crystals, but, for many of the applications envisaged in integrated optics or fibre optics, the materials would be in the form of thin films or fibres.

Second-harmonic-generation (SHG) measurements on powdered samples are frequently used to determine the potential of compounds as frequency-doubling crystals. The method was originally described by Kurtz and Perry [3, 4]. The response from a powdered sample depends on the crystal size, orientation and on the extent of the refractive-index match between the powder and any suspending liquid.

Our particular interest is in the possibility of producing composite materials by methods analogous to those by which mineralization occurs in biological composites such as bone. In this case a preformed swollen organic matrix becomes supersaturated with

an inorganic compound which precipitates [5]. The presence of the matrix affects the size and orientation of the crystals and limits the extent to which aggregation can take place, in distinction to precipitation from solution. The method which we have adopted involves the casting of films from a solution containing both an organic or inorganic compound and a polymer in a mutual solvent. The crystalline precipitate may form either during the drying of the solvent or during a subsequent annealing cycle. The angular distribution of the SHG emission is dependent on the morphology of the composite. We are investigating the possibility that SHG studies may provide a sensitive probe for the internal structure of the composites.

Two related organic crystals were studied, 2-methyl-4-nitroaniline (MNA) and 3-nitroaniline (mNA) [6, 7]. Both are reported to have exceptionally high non-linear optical coefficients. The compounds were dissolved in toluene in various proportions with either polymethylmethacrylate (PMMA) or polystyrene (PS). Films were cast by dipping a microscope slide into the solution and allowing the solvent to evaporate at 60°C . These films were all $5 \pm 1\ \mu\text{m}$ thick.

Composites of potassium dihydrogen orthophosphate (KDP) and of ammonium dihydrogen orthophosphate (ADP) in polyethylenoxide (PEO) were prepared by evaporation of aqueous solutions. These films were $100\ \mu\text{m}$ thick.

SHG measurements were made using a Spectron

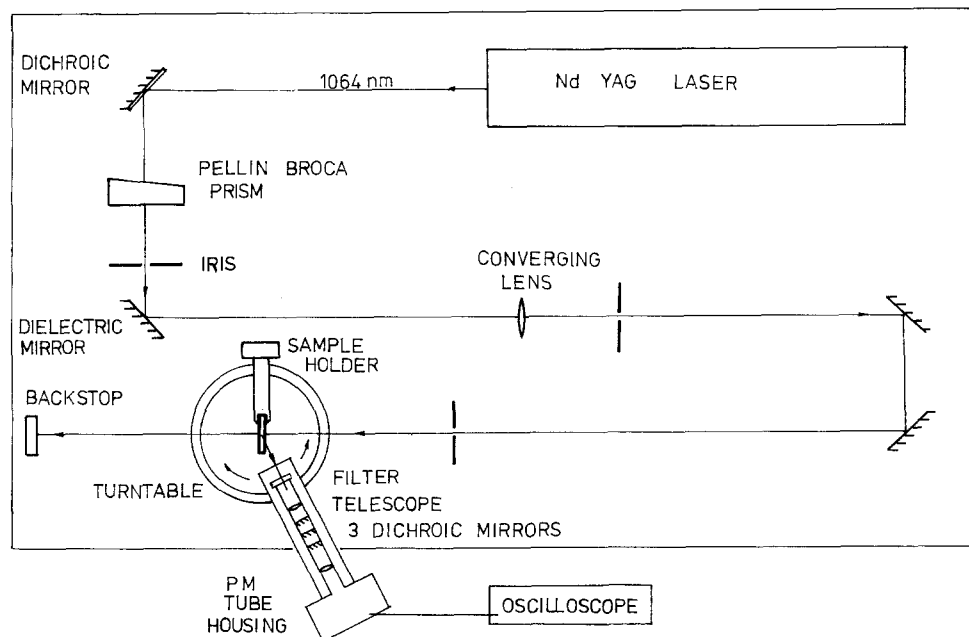


Figure 1 Diagram of experimental apparatus.

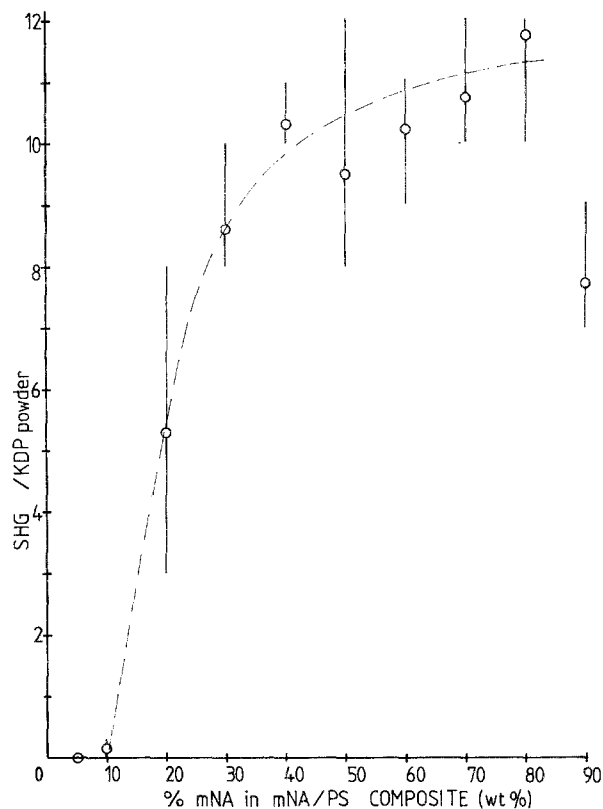


Figure 2 Plot of SHG against composition for mNA-polystyrene composites.

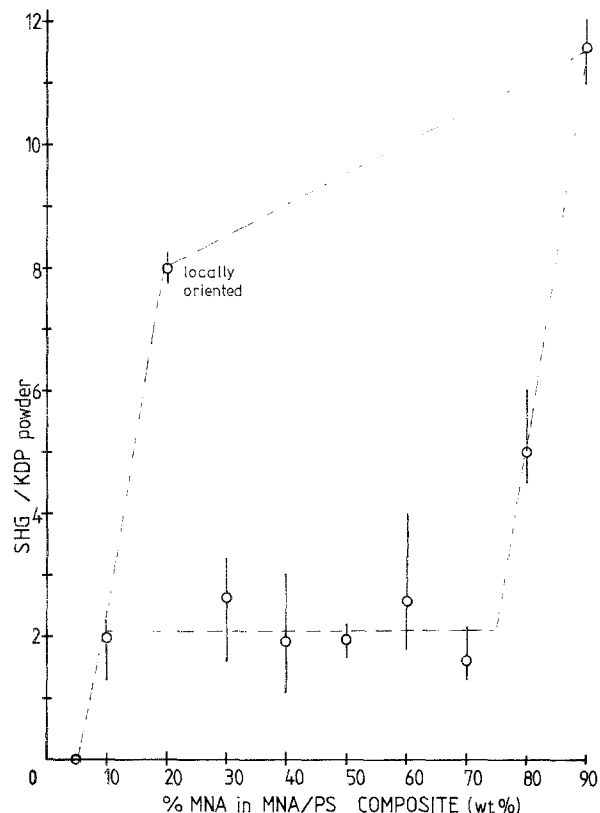


Figure 4 Plot of SHG against composition for MNA-polystyrene composites. Regions of fibrous crystals show higher SHG.

SL2Q Nd-YAG laser operating at $1.06 \mu\text{m}$. The green 532 nm emission was detected by a Hamamatsu 1P28 photomultiplier coupled to a Hewlett Packard 1744A 100 MHz storage oscilloscope. The oscilloscope monitored the photomultiplier current as the voltage across a $1 \text{ M}\Omega$ resistance. The photomultiplier was fitted with a telescope such that light was accepted over an angular range of $\pm 5^\circ$ at a distance of 10 cm from the sample. The illuminated area of the sample was

1 mm^2 . A series of filters and dichroic mirrors in the viewing telescope were used to eliminate the $1.06 \mu\text{m}$ radiation transmitted by the sample. The samples were mounted with the films between glass slides and covered by a layer of paraffin oil in order to reduce surface scattering effects. In the absence of any crystalline sample, no SHG signal was detected. The experimental arrangement is shown diagrammatically in Fig. 1.

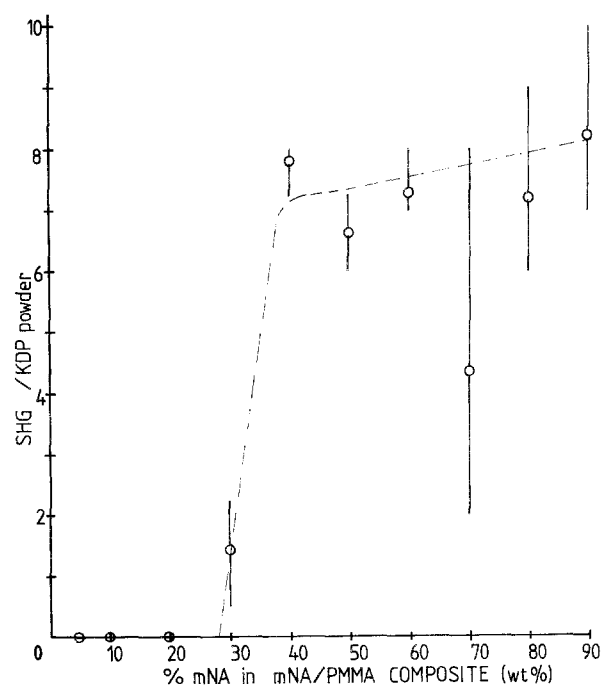


Figure 3 Plot of SHG against composition for mNA-polymethylmethacrylate composites.

Figs 2 and 3 show the SHG output from composites of 3-nitroaniline in polystyrene and in polymethylmethacrylate. In each case the intensity is zero up to some critical concentration above which it rises steeply and then levels off. Microscopic examination showed that the critical level corresponded to that at which crystals first appeared in the polymer and, hence, to the solubility of the nitroaniline in the polymer.

The absolute measurement of SHG intensities is difficult, but it is customary to compare compounds with a simple reference material. The values quoted are relative to intensities measured on powdered samples, $250 \pm 10 \mu\text{m}$ thick, of potassium dihydrogen orthophosphate. All measurements, unless otherwise stated, were taken in transmission (180°).

Figs 4 and 5 show the concentration dependence of SHG from films containing MNA in polystyrene or polymethylmethacrylate. The solubility of this material is lower and so the concentration at which SHG starts is also quite small. The pattern of the intensity change is also quite different in that the emission rises to a plateau and then rises again at high concentrations. By optical microscopy, we observe a different pattern of crystallization for MNA as compared to mNA. In

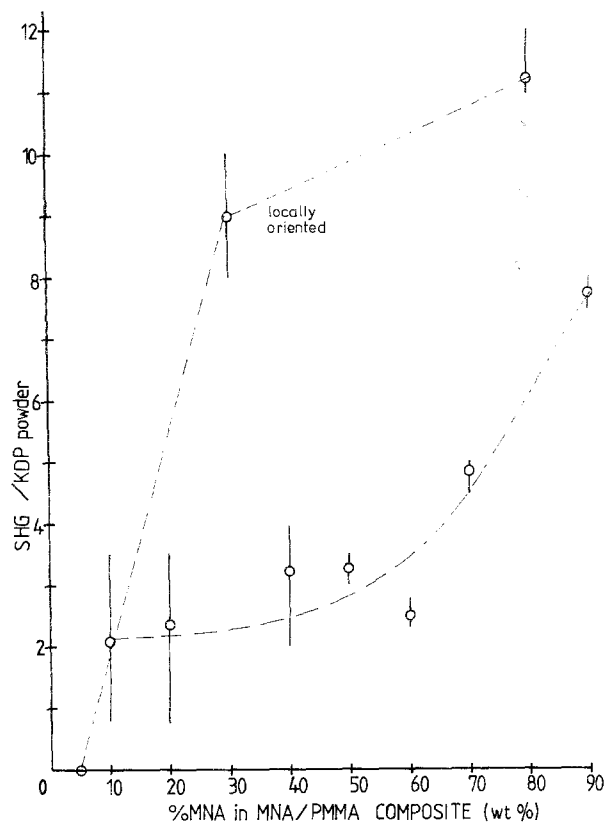


Figure 5 Plot of SHG against composition for MNA-polymethylmethacrylate composites.

MNA the crystals appear as a fine mat of unoriented particles with a size range on the limit of resolution, less than $1\ \mu\text{m}$. In mNA the crystals have the form of larger needles of about $10\ \mu\text{m} \times 1\ \text{mm}$ which are arranged in spherulites. These large spherulites give the samples an overall high level of local orientation

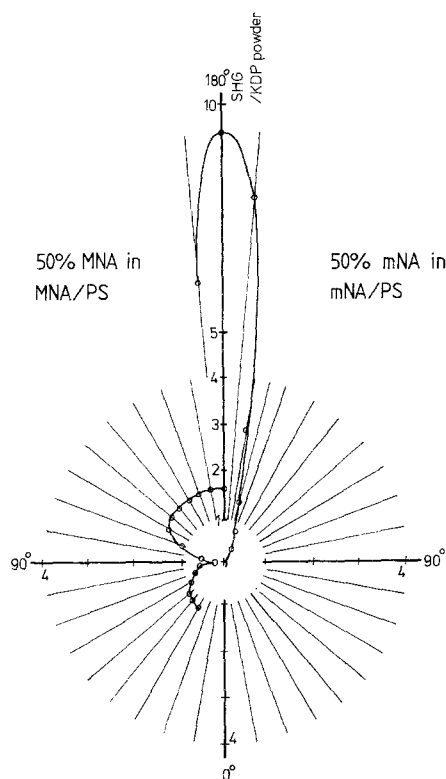


Figure 6 Angular dependence of SHG for mNA- and MNA-polystyrene composites. Transmission direction is 180° .

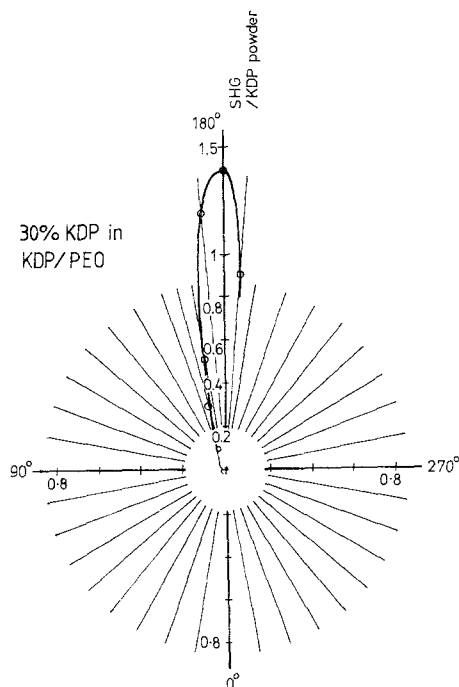


Figure 7 Angular dependence of SHG by KDP-polyethyleneoxide composites.

and we believe that this causes the initially rapid rise in SHG with concentration. With both mNA and MNA this is a considerable scatter in the results which arises from morphology differences between different points on the films. As shown in Figs 4 and 5, higher values of SHG emission in the forward (180°) direction are associated with regions where the structure shows local orientation. Similar large scatter has been reported for measurements on powders [3]. The maximum level of SHG emission is similar to that observed from powdered samples, $250 \pm 10\ \mu\text{m}$, of the nitroanilines alone.

Kurtz and co-workers [3, 4] discuss the angular dependence of the SHG intensity in terms of the refractive-index match between the suspending fluid and the SHG crystals. They show that with a poor refractive-index match the strong scattering will result in second-harmonic emission occurring as two equally sized lobes in the forward and reverse directions. In the case of a good match most of the second harmonic is concentrated in the forward direction and very close to the main beam. In our samples the refractive index of the nitroanilines is about 1.8 [6, 8], whereas that of the embedding polymer is close to 1.5 so the match is very poor. Nonetheless, we find that with mNA the emission is quite strongly concentrated in the forward direction, whereas with MNA the SHG is distributed over two lobes, as shown in Fig. 6. We believe that this arises because the mNA crystals grow as parallel fibres, not as uncorrelated powders. A similar narrow lobe of SHG emission is seen in the system potassium dihydrogen orthophosphate-polyethyleneoxide (Fig. 7).

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