

Fig. L.12.1 Schematic diagram of CVD reactor



Fig.L.12.2 Stand-alone ZnS after polishing in different shape

Inert carrier gas (argon) is passed over molten Zn (~600°C) contained in a graphite pot, to pick up Zn-vapour, and fed into the base of the reactor. High-purity H₂S gas, along with the inert carrier gas, controlled through mass flow controllers and meters, is also fed into the base of the reactor. The chemical reaction leads to the formation of ZnS that gets

deposited on the walls of the cylindrical reactor, as well as on the substrate kept at the top of the reactor. Un-reacted or excess Zn remaining in the gas stream is dumped into the carbon dump box above the growth box mandrel before the effluent gas is removed from the CVD reactor by a rotary vacuum pump. The effluent gas is sterilized of any residual H₂S gas by passing it through a scrubbing tower with a spray of sodium hydroxide (NaOH) solution. The treated gas is tested for any H₂S traces and then let out into the atmosphere through a tall chimney. Good quality blanks were obtained at ZnS deposition rate of the order of 1 μm/minute. X-ray diffraction measurements on ZnS blanks confirmed cubic structure with a lattice parameter of 5.405 Å. Microstructure study using the scanning electron microscope and atomic force microscopy revealed no porosity and average grain size of ~50 nm for a ~0.6mm thick ZnS blank

Figure L.12.2 shows a picture of free-standing, ZnS blank and dome. Both the blank and dome can be seen to have good transparency. The transmission spectrum of a ~2.0 mm thick flat blank in the 8-12 μm wavelength range is shown in Fig. L.12.3. The measured transmission value of ~70% compares well with the commercially available blanks. The measured density of the blank (~4.10 gm/cc) and its Vicker's hardness (~200) was also comparable to reported values.

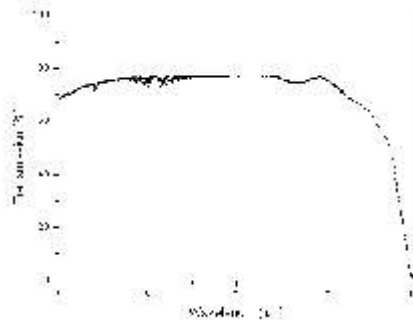


Fig.L.12.3: Transmission spectrum of transparent ZnS blank

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L.13 : Nonlinear optical studies in neutral red dye under nanosecond laser pulse excitation

In the recent past, rapid technological advancements in optics have placed great demand on the development of nonlinear optical materials suitable for photonic devices. Organic chromophores exhibit versatility of synthesis, their nonlinear optical (NLO) properties can be custom-tailored for a specific application. One of the important applications of these materials is in optical limiting devices used to protect

eyes and sensors against damage by exposure to sudden high intensity light, which still remains a challenging problem. Investigations on the nonlinear absorption, nonlinear refraction and optical limiting (OL) response of the organic chromophore, neutral red (NR) under nanosecond pulsed laser light irradiation at 532 nm was studied. NR (3-amino-7-dimethylamino-2-methyl phenazine) is a low cost organic dye which finds many applications in biology. Z-scan experiments and nonlinear transmission measurements were carried out to investigate the NLO properties and OL behaviour, respectively, of the dye chromophore.

The Z-scan experiments were conducted employing frequency doubled pulsed Nd:YAG laser light (532 nm, 30 ns) with a repetition rate of 1 Hz in a 1 mm quartz cuvette. Both closed and open aperture Z-scan measurements were performed, simultaneously. Optical limiting experiments were also performed with NR solution. Fig.L13.1 illustrates the open aperture Z-scan data, of NR solution in methanol (linear transmission 20 % at 532 nm). At a peak incident laser intensity of 130 MW/cm², the spot size of the beam being ~ 35 μm, it exhibits an interesting behaviour. The sample shows saturable absorption behaviour away from focus and reverse saturable absorption behavior near the focus. To estimate the saturation intensity and the nonlinear absorption coefficient, the experimental data was fitted with numerical simulations and is shown by solid line. Theoretical fit gives saturation intensity, $I_s = 18 \text{ MW/cm}^2$ and two photon absorption (TPA) coefficient, $\beta = 110 \times 10^{-8} \text{ cm/W}$. Estimated β value in NR solution is very large compared to recently reported β values in various dyes viz., Rubrene, Eosin, Pyridin1, Fluorescein 27, Rhodamine 6G and Rhodamine B

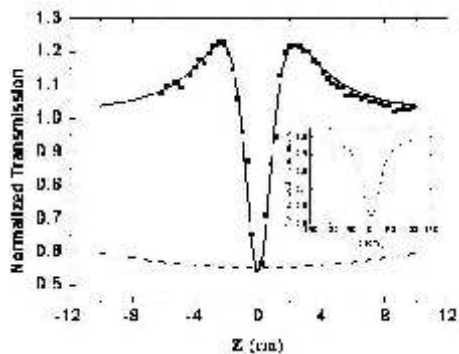


Fig.L.13.1: Open aperture Z-scan experimental data (squares) of NR solution in methanol at $I_0 = 130 \text{ MW/cm}^2$. Solid line shows theoretical fit to the experimental data. Dashed line shows theoretical curve considering excited state absorption. Inset shows dashed curve for large Z-values.

Further, attempt was made to fit the experimental data with excited state absorption to rule out its possibility. For

excited state absorption, rate equations were solved to estimate the magnitude of the excited state absorption cross-section (σ_2). Dashed line shown in Fig.L.13.1 was generated for the excited state absorption cross-section $\sigma_1 = 9.2 \times 10^{-17} \text{ cm}^2$, $\sigma_2 = 13.25 \times 10^{-17} \text{ cm}^2$ and $\beta = 0$, to match the dip in the transmission of the experimental data. The theoretically estimated complete normalized transmission curve does not appear within the experimentally used Z-values. The complete dashed curve is shown in the inset of Fig.L.13.1 and was generated with Z values much larger than that used in the experimental data. Obviously, the dashed curve does not fit to the experimental data. The saturation of absorption is also included in the analysis, but no peak is observed in the transmission curve. Therefore, it was concluded from the analysis that the dominant mechanism of nonlinear absorption in neutral red dye is TPA.

The estimated value of nonlinear refractive index, n_2 , of the sample by fitting closed aperture Z-scan data was found to be $1.5 \times 10^{-12} \text{ cm}^2/\text{W}$, while in the solid film form, it was $4.0 \times 10^{-9} \text{ cm}^2/\text{W}$. The larger value of n_2 in the solid form of NR sample may be due to the greater concentration of NR dye molecules in the solid film ($\sim 10^2 \text{ mol/L}$) compared to the solution ($\sim 10^4 \text{ mol/L}$). The observed optical limiting of nanosecond laser pulses at 532 nm showed that, neutral red, which has a limiting threshold lower than that of C₆₀, is a good optical limiter. Moreover, the simultaneous occurrence of several nonlinear processes in this dye, signifies the possibility of utilising it in photonic device applications.

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L.14 : Polarization dependence of quadratic photocurrent in light emitting diodes

Semiconductor devices like photo-diodes, laser diodes, light emitting diodes etc. have drawn considerable interest in recent years as simple, easy to use, and inexpensive substitute for second harmonic generation (SHG) based non-linear crystals for several applications like autocorrelation measurements of ultra short laser pulses, ultra high-speed optical communication, microscopy etc. Knowledge of the polarization dependence of the induced quadratic photocurrent in the former is essential in certain applications such as polarization-insensitive cross correlation measurements or fringe-free cross-polarized autocorrelation (CP-AC) used in collinear optical geometry for microscopy. Although the exact physical process responsible for quadratic photocurrent in light emitting diodes (LED) is not known precisely, it is generally assumed to be due to the two-photon absorption (TPA) process in the