

## THERMALLY SWITCHABLE LASER DIFFRACTING GELS

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**ABSTRACT:** Colloidal crystalline array (CCA) of dyed fluorinated organic spheres empedded in an acrylamide hydrogel matrix is made to Bragg diffract a laser beam (probe) by another laser beam (pump) that heats up the spheres. CCA is nearly refractive index matched with the medium of water and dimethyl sulphoxide (DMSO) so that only about 0.7 % of probe intensity is diffracted. Upon shinning the pump beam on the CCA, dye absorbs the pump, heats up the spheres to decrease the refractive index. This results in the increased refractive index mismatch and the CCA diffracts more probe intensity of about 2 %. The CCA cools back and ceases to diffract the probe beam in about 10 ns when the pump beam pulse is of the order of 3.5 ns.

### 1. INTRODUCTION

Highly charged, monodisperse organic or inorganic colloidal spheres self-assemble in a periodic array of body centered cubic (BCC) or face centered cubic (FCC) structures in a polar medium like water under the conditions of high sphere concentration and low ionic strength[1]. This colloidal crystalline array (CCA) is the result of the electrostatic interparticle interaction[2] and diffracts the visible light that meets the Bragg condition

$$m\lambda = 2nds\sin\theta \quad (1)$$

where  $m$  is the order of diffraction,  $\lambda$  is the wavelength of light,  $n$  is the suspension refractive index,  $d$  is the interplanar spacing and  $\theta$  is the Bragg angle between the incident light and the diffracting crystal planes which are oriented parallel to the crystal surface in the CCA we prepare[3]. The diffracted intensity depends on the refractive index mismatch between the colloidal particle and the surrounding medium, the wavelength of light, particle diameter and the defects in the CCA. Such arrays can be used as narrow band optical rejection filters[1,4] and have been proposed in novel nonlinear optical switching applications[5,6].

These CCAs are highly fragile that a shear force caused by a convection in the medium

or a gentle agitation of the container can melt them, since they have low elastic modulus of about 100 dynes/cm<sup>2</sup> [7]. In order to make good devices, CCAs are to be quite rigid. These CCAs can be locked up in their ordering by polymerising the acrylamide hydrogel around the CCAs[8,9]. These polymerised CCAs (PCCAs) withstand agitation, ionic impurity addition and thermal shocks and continue to diffract light.

We proposed that CCA self-assemblies could be used as nanosecond optical switching devices which utilize the temperature dependence of the particle refractive index[5,6]. We demonstrate here the optical switching of a probe laser beam meeting the Bragg condition in a PCCA, when a pump laser beam heats up the dyed colloidal particles array which is nearly index matched with the medium.

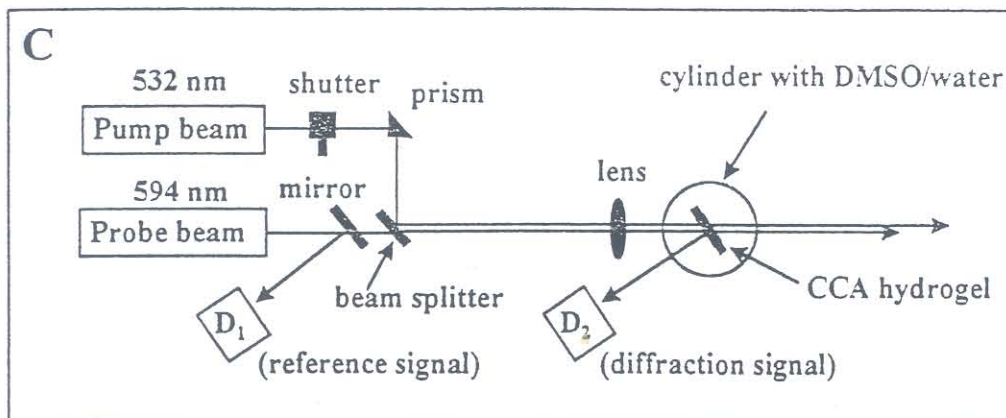
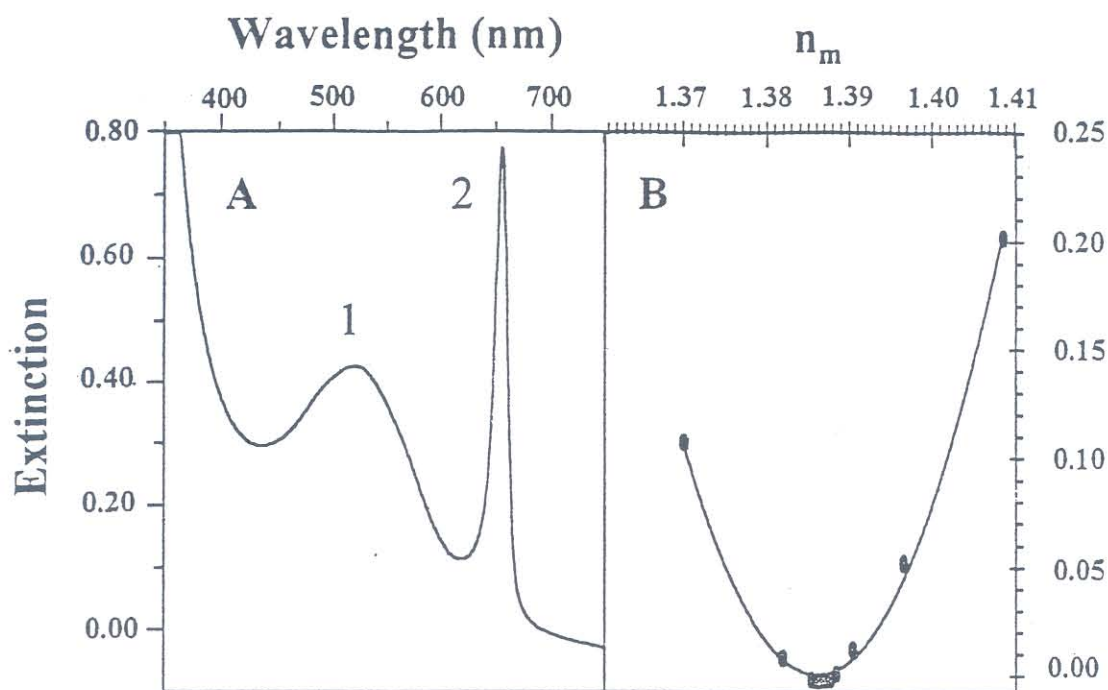
## 2. EXPERIMENTAL

We synthesized the charged monodisperse colloidal particles of heptafluorobutyl methacrylate and covalently attached acrylated Oil Blue N dye to these colloidal spheres. Acrylated Oil Blue N dye absorbs the light in the wavelength range of 530 nm and does not fluoresce. These particles were prepared by emulsion polymerization of 10 g 1,1-H<sub>2</sub>heptafluorobutyl methacrylate monomer, 0.1 g Aerosol MA 80-I surfactant, 0.0032 g Acrylated Oil Blue N dye, 0.16 g sodium persulfate free-radical initiator and 20 g deionised water at 55 °C for 3 hours. The colloid was purified after synthesis by dialysis against ultrapurified water and subsequent mixing with mixed bed ion exchange resins. The particle diameter was obtained from TEM as 138 nm and the charge, 2300e (e is the electronic charge), from measuring the suspension electrical conductivity at various volume fractions of the spheres. These spheres have the lowest refractive index ( $n_p=1.386$ ) of any monodisperse colloidal spheres known. Such a low refractive index colloid is preferable to index match with the medium. CCA orders well in aqueous medium since water is highly polar with dielectric constant, 78.4, and the refractive index  $n_w=1.333$ . In order to index match the medium with the colloid, we need to add a high refractive index solvent which is compatible with water and the particle such as dimethyl sulphoxide (DMSO,  $\epsilon=45, n_d=1.477$ ). However, CCA begins to disorder with large amount of DMSO due to the decrease of the particle charge. This requires low refractive index colloid.

The dyed fluorinated colloidal spheres self-assemble into CCA which are then polymerised within the acrylamide hydrogel. The polymerised CCA (PCCA) was prepared by photopolymerisation of an ordered aqueous dispersion of 1.58 g of the spheres of 11 % w/w solid, 1.93 g ultrapure water, 0.345 g acrylamide monomer, 0.023 g N,N'-methylene bisacrylamide cross-linker, and 0.002 g diethoxyacetophenone UV photoinitiator between two quartz plates separated by a 800  $\mu$ m thick parafilm spacer at 25 °C. The above mixture was purified by mixed bed ion exchange resins to achieve CCA self-assembly. After photopolymerisation, PCCA was cleaned with deionised water.

Figure 1A shows the optical extinction spectra of the PCCA. The broad 530 nm band results from the colloidal particles dye absorption and the sharp 640 nm peak results from the CCA Bragg diffraction. DMSO was added to the mainly aqueous medium of the PCCA to adjust the medium refractive index ( $n_m$ ) to either slightly above or below that





### Pump-probe experimental setup

Fig.1: A::Transmission spectrum of charged 138 nm diameter dyed poly(heptafluorobutyl methacrylate) PCCA in water. Peak 1 is the absorption band of acrylated Oil Blue N dye which is covalently bonded to the particles, peak 2 is the CCA Bragg diffraction band. The spectrum was recorded in a UV - visible - near IR spectrophotometer with the PCCA placed normal to the incident light beam.

B::The optical extinction of the dyed PCCA as measured from the peak 2 of the transmission spectra (A) for various medium refractive indices. The data (filled circles) is fitted to a parabolic curve (solid line). C:: Schematic pump - probe experimental setup. 800  $\mu\text{m}$  thick PCCA was mounted on an aluminium metal frame which was placed in a glass cylinder containing a mixture of DMSO and water. The 532 nm pump beam and the 596 nm probe beam were collinear and focused at the PCCA. The incident probe intensity is proportional to the  $D_1$  photodiode reading and  $D_2$  photodiode reads the diffracted probe intensity.

of the particles ( $n_p$ ). The Bragg diffraction peak height decreases as the refractive index mismatch between the medium and the particle ( $n_m - n_p$ ) decreases. The mismatch is negative for the PCCA equilibrated in water and when DMSO is added continuously, its magnitude decreases, becomes zero, then becomes positive and increases. Figure 1B shows the Bragg diffraction peak height as a function of the medium refractive index. The data fits to a parabola. The extinction does not become zero at zero mismatch due to the optical anisotropy of the fluorinated particles and the complex refractive index of the dye.

Figure 1C shows the schematic experimental setup used to monitor the diffraction of the probe beam from the PCCA upon pump beam heating. The 532 nm pump beam of 3.5 ns pulse duration was derived from a Coherent Inc. Infinity YAG laser by frequency doubling. This beam was absorbed by the dyes in the colloidal spheres to heat them. The 596 nm probe beam of same duration was derived from a dye laser pumped by the 532 nm beam. The pump and the probe beams were made collinear and focused to about 100  $\mu\text{m}$  spot size on the sample. The probe was delayed with respect to the pump by 2.5 ns[5]. The 800  $\mu\text{m}$  thick PCCA was mounted on a metal frame so that the hydrogel face with the highest density CCA plane was perpendicular to the scattering geometry. The sample was immersed in a cylindrical bath of water and DMSO mixture to reduce the scattering and to adjust the refractive index mismatch to any desired value. The relative angle of the sample to the probe beam was adjusted to about  $20^\circ$  such that the Bragg condition was met.

Various time delays between the pump beam and the probe beam were introduced by varying the path length of the pump beam. The spot size of the beams was measured using a razor blade. The refractive index of the suspension was measured using an Abbe refractometer at any desired temperature and that of the particle was estimated from the particle volume fraction.

### 3. RESULTS AND DISCUSSION

The probe beam of 596 nm, derived from the dye laser which was pumped by a part of the 532 nm beam of frequency doubled YAG laser, was diffracted by the PCCA using the setup shown in Fig. 1C. The intensity was measured using a fast response photodiode,  $D_2$ . The pulse width of the laser beams (3.5 ns) were measured using fast oscilloscope. The



diffracted intensity was normalised to the incident probe intensity as measured by the fast responsive photodiode,  $D_1$ . This ratio,  $R_{off}$ , was obtained when the pump beam was not shinned on the PCCA. Then, the pump was shinned on the PCCA and the ratio,  $R_{on}$ , of the probe diffracted intensity to the incident intensity was obtained. Figure 2 shows the ratio(signal) between the diffracted probe intensity from the PCCA before and after the PCCA was heated by the pump ( $R_{on}/R_{off}$ ) for various pump intensities. The probe was delayed by 2.5 ns as compared to the pump by adjusting their relative path length. The pump beam heated up the spheres in the PCCA and their refractive index decreased. This changed the refractive index mismatch between the sphere and the medium and caused the signal to vary. The signal increases on heating the PCCA when it is over-index matched ( $n_m$  (1.3902)  $n_p$  (1.386)); but decreases when under-index matched ( $n_m$  (1.3817)  $n_p$ ). The over-index matched PCCA deviates more and more from the perfect index matching upon pump intensity increase which results in signal increase. On contrary, the under-index matched PCCA would approach the perfect index matching upon heating which results in signal decrease. Also shown in Fig. 2 is the signal for the PCCA having undyed spheres. As expected, PCCA without dye can not be heated up using the pump laser beam and hence the signal remains at 1 for all pump intensities.

In Fig.2, the signal from the over(under)-index matched PCCA drops (increases) after ca. 570  $\mu\text{J}$  pump intensity. This means that the pump heating-induced refractive index mismatch,  $\delta n$  ( $=n_m - n_p$ ), decreases (increases) in magnitude for over (under)-index matched PCCA at 570  $\mu\text{J}$ . This can occur if  $n_m$  decreases or  $n_p$  increases discontinuously at 570  $\mu\text{J}$  pump intensity. We calculated from the pump beam transmission that ca. 34 % of the pump intensity was absorbed in the PCCA. About the same value was obtained from the extinction due to the dye absorption at 532 nm as read from Fig.1A. Assuming that this energy is absorbed by the spheres, the sphere temperature increase,  $\delta T$ , was calculated as 44  $^\circ\text{C}$  at 570  $\mu\text{J}$  pump intensity. This corresponds to the sphere temperature of 67  $^\circ\text{C}$  as a result of the heating of the sphere with the pump beam of 570  $\mu\text{J}$ . The variation of polymer specific heat with temperature shows a jump at 62  $^\circ\text{C}$  as shown in Fig. 3A. This temperature is the glass transition temperature,  $T_g$ , of the particle. In Fig.3A, the particle specific heat starts to increase at 58  $^\circ\text{C}$  which corresponds to the onset of glass transition. Fig.3B shows the particle refractive index as a function of temperature; the slope change occurs at 58  $^\circ\text{C}$  which is the onset of glass transition. The signal in Fig.2 varies monotonically till the particle temperature reaches  $T_g$  at 570  $\mu\text{J}$  pump intensity. The calculated value of 67  $^\circ\text{C}$  at 570  $\mu\text{J}$  is 5  $^\circ\text{C}$  higher than  $T_g$  since the particle cooling in 2.5 ns probe delay time has not been considered in the calculation.

The specific heat curve, in Fig.3A, shows a peak at 67  $^\circ\text{C}$  which is presumably due to the melting of the possible polymer crystalline order. This melting would have been resulted by the stress due to glass transition of the amorphous region of the polymer sphere. The sudden particle volume decrease accompanying the melting at 67  $^\circ\text{C}$  results in sudden  $n_p$  increase and  $n_m$  decrease. This causes the observed signal drop (increase) in the over (under)-index matched PCCA.

In Fig.2, the signal from the over(under)-index matched PCCA continues to increase

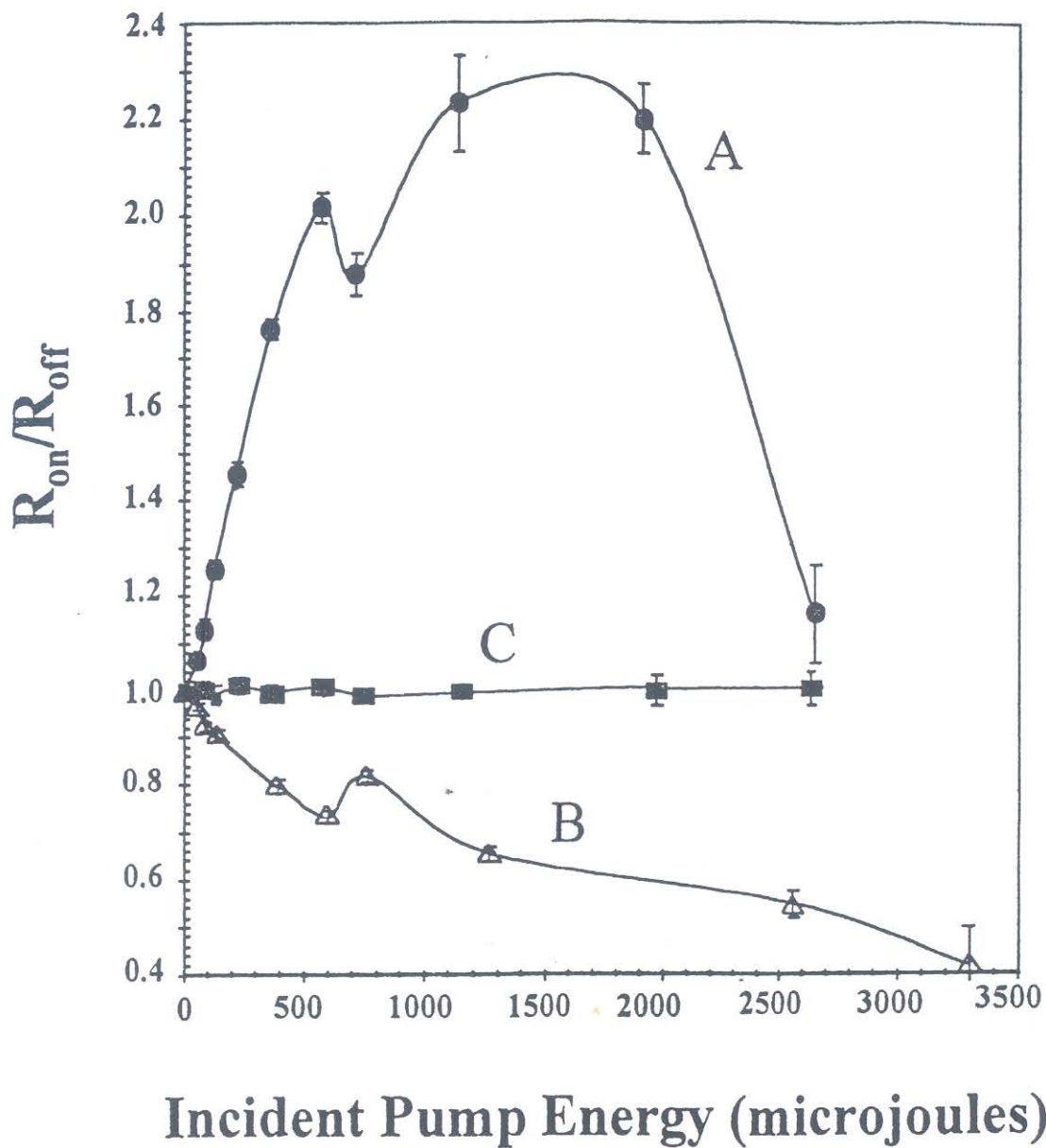


Fig. 2. Pump beam energy dependence of  $R_{on}/R_{off}$  at both over and under-index matching conditions. Curve A and B were measured on a dyed PCCA with  $n_m$  adjusted to 1.3902 and 1.3817, respectively; Curve C was measured on an undyed PCCA at  $n_m = 1.3874$ .

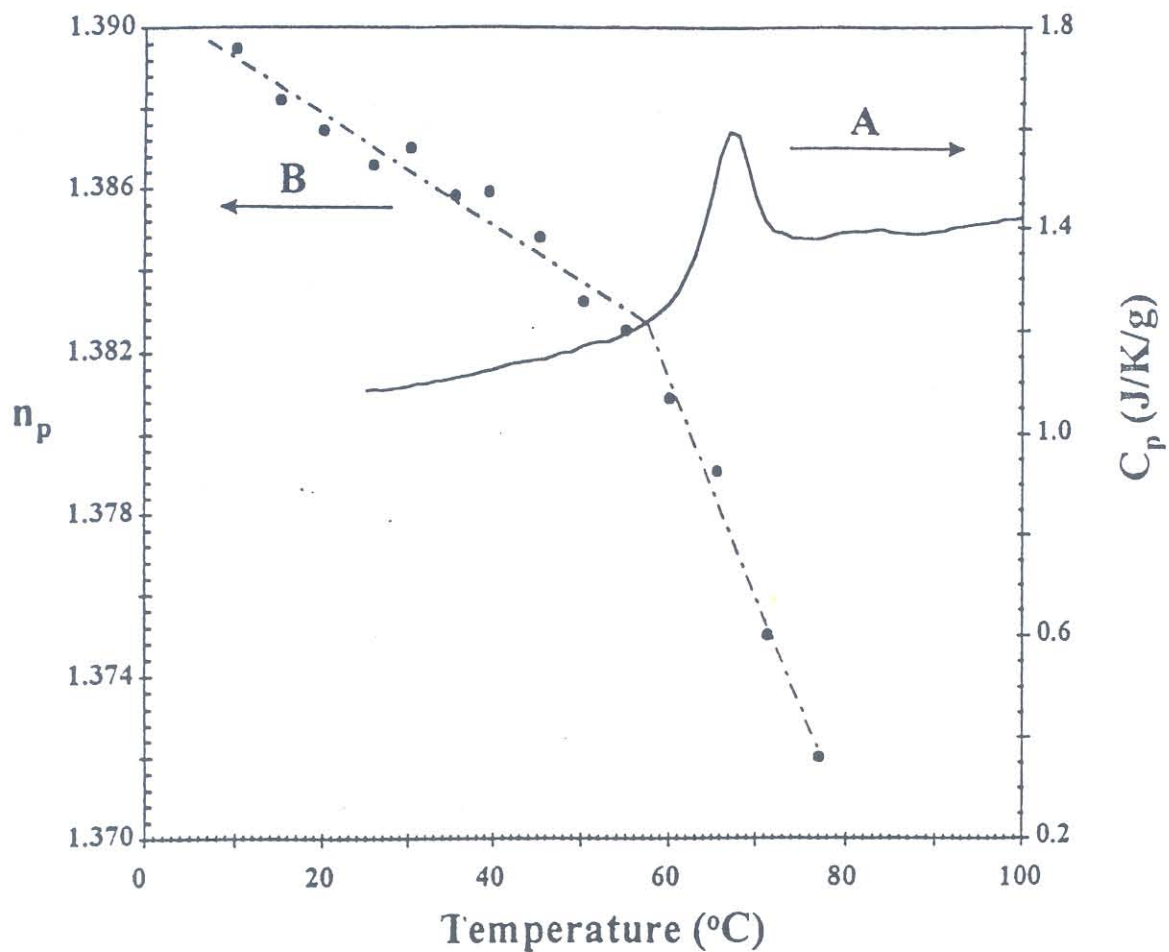


Fig. 3. A: Temperature dependence of the polymer specific heat capacity. The onset of the glass transition occurs at  $58^{\circ}\text{C}$ .  $T_g = 62^{\circ}\text{C}$ . The peak at  $67^{\circ}\text{C}$  represents the melting of the crystalline fraction of the colloidal polymer. B: Temperature dependence of the particle refractive index.  $dn_p/dT = -1.39 \times 10^{-4} / ^{\circ}\text{C}$  changes at  $58^{\circ}\text{C}$  to  $-5.40 \times 10^{-4} / ^{\circ}\text{C}$ .



(decrease) after the drop (increase) at  $T_g$  till about 1500  $\mu\text{J}$  pump intensity due to the continuous change in the pump induced index mismatch. After 1500  $\mu\text{J}$ , the colloidal particles are damaged and the colloidal crystalline array is destroyed. Hence, the signal decreases. The SEM pictures of the particles heated by 2000  $\mu\text{J}$  pump intensity when the particles were dispersed in the suspension confirm the particle damage. Fig.2 is repeatable if the pump intensity is below 1500  $\mu\text{J}$ . After this intensity limit, PCCA is irreversibly damaged.

We found that the features of a first peak and a broad second peak shown in Fig.2 appear at lower pump energies if the pump is focused to a smaller size, as expected. When the probe preceded the pump by 2.5 ns, the diffracted probe intensity does not change with the pump intensity because pump falls after the probe intensity vanished on the PCCA. If probe and pump fall on the PCCA at the same time, the signal is only 50% of the probe signal for 2.5 ns probe delay. If the probe is delayed by more than 2.5 ns, the signal falls again due to the cooling of the PCCA during the delay time.

The maximum reversible pump heating of the PCCA results in ca. 3 times larger when the pump is off. This increase in the probe diffracted intensity corresponds to ca.2% of the incident probe intensity. Further work is in progress to diffract more probe intensity.

#### 4. CONCLUSION

This PCCA functions as a nanosecond optical switch; the switch is activated by a pump beam. It can switch simultaneously many probe beams of different wavelengths meeting Bragg condition at different incident angles. 3 fold increase of the diffracted probe intensity is enough to make the switching logic unmistakable. This PCCA would be even more interesting if it diffracts a sizable fraction of the incident probe intensity.

#### REFERENCES

- [1] I. M. Krieger and F. M. O'Neill, *J. Am. Chem. Soc.* **90**, 3114 (1968); P.A. Hiltner and I.M. Krieger, *J. Phys. Chem.* **73**, 2386 (1969).
- [2] E.J.W. Verwey and J.Th.G. Overbeek, Theory of the Stability of Lyophobic Colloids (Elsevier, Amsterdam, 1948).
- [3] R.J. Carlson and S.A. Asher, *Appl. Spectros.* **38**, 297 (1984).
- [4] S.A. Asher, U.S. Patents 4 627 889 and 4 632 517 (1986).
- [5] R. Kesavamoorthy, M.S. Super and S.A. Asher, *J. Appl. Spectros.* **71**, 1116 (1992).
- [6] S.A. Asher, S.-Y. Chang, S. Jagannathan, R. Kesavamoorthy and G. Pan, U.S. Patent 5 452 123 (1995).
- [7] R.S. Crandall and R. Williams, *Science* **198**, 293 (1977); R. Kesavamoorthy and A.K. Arora, *J. Phys. A: Math. Gen.* **18**, 3389 (1985).
- [8] G. Haache, H.P. Panzer, L.G. Magliocco and S.A. Asher, U.S. Patent 5 266 238 (1993); S.A. Asher and S. Jagannathan, U.S. Patent 5 281 370 (1994)
- [9] J.M. Weissman, H.B. Sunkara, A.S. Tse and S.A. Asher, *Science* **274**, 959 (1996).