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Third Order Optical Nonlinearity of Colloidal Metal Nanoclusters Formed by MeV Ion Implantation

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THIRD ORDER OPTICAL NONLINEARITY OF COLLOIDAL METAL NANOCLUSTERS FORMED BY MeV ION IMPLANTATION

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ABSTRACT

We report the results of characterization of nonlinear refractive index of the composite material produced by MeV Ag ion implantation of $LiNbO_3$ crystal (z-cut) The material after implantation exhibited a linear optical absorption spectrum with the surface plasmon peak near 430 nm attributed to the colloidal silver nanoclusters Heat treatment of the material at 500°C caused a shift of the absorption peak to 550 nm The nonlinear refractive index of the sample after heat treatment was measured in the region of the absorption peak with the Z-scan technique using a tunable picosecond laser source (4 5 ps pulse width). The experimental data were compared against the reference sample made of MeV Cu implanted silica with the absorption peak in the same region The nonlinear index of the Ag implanted $LiNbO_3$ sample produced at five times less fluence is on average two times greater than that of the reference

1. Introduction

Solids containing metal colloidal nanoclusters are of great interest due to their nonlinear optical properties [1 -7] The third-order optical susceptibility is large, and the nonlinear optical

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response time is in the picosecond regime Ion implantation has been shown to produce a high density of metal colloids in glasses and other materials The high-precipitate volume fraction and small size of nanoclusters leads to values for the third-order susceptibility much greater than those for metal doped solids [2, 3, 4, 6] This has stimulated interest in use of ion implantation to make nonlinear optical materials On the other side, $LiNbO_3$ has proved to be a good material for optical waveguides produced by MeV ion implantation [8, 9] Light confinement in these waveguides is produced by an optical isolation barrier with low refractive index in nuclear stopping region of the ions Implantation of $LiNbO_3$ with MeV metal ions can therefore result into nonlinear optical waveguide structures with great potential in a variety of device applications [10] We present the results of characterization of linear absorption and nonlinear refractive index of $LiNbO_3$-based composite material produced by silver ion implantation

2. Experimental

The sample was made of 1-mm thick $LiNbO_3$ (z-cut) implanted with 1.5-MeV Ag ions to a dose of $2\ 0\times10^{16}\,\mathrm{cm}^{-2}$ Implantation was done at room temperature. Fig 1 presents the distribution of the implanted silver along the depth of the sample calculated by the Monte-Carlo simulation program TRIM96 [11] The position of the peak of the distribution defines the depth of the implanted layer at 0 41 μm and FWHM of the distribution gives an estimate of 0.24 μm for the thickness of the layer

The linear optical absorption spectra of the implanted sample are shown in Fig 2 The spectrum right after implantation exhibits the prominent single surface plasmon peak near 430 nm which is the signature of nanometer size clusters of metallic silver formed in the host The radius of the clusters can be estimated by using the relation $R = V_f/\Delta\omega_{1/2}$, where V_f and $\Delta\omega_{1/2}$ are Fermi's velocity of silver (1.39×10^8 cm/s [12]) and the half width of the absorption peak, respectively [13] In our case $R \approx 1\ 1$ nm. Heat treatment after the implantation at 500°C for 1 hour lead to the red shift of the absorption peak to 550 nm (Fig 2) without significant change of $\Delta\omega_{1/2}$ (and, correspondingly, of the radius R). Shang, et al proposed to explain this effect as a result of the volume fraction increase due to Ag precipitation near the surface [14] Another likely contributing factor is that the heat treatment is working to remove implantation damage [15] $LiNbO_3$ implanted with 190 keV Ag at $1x10^{17}$-cm^{-2} fluence has been shown to undergo full epitaxial regrowth after heat treatment at 400°C but an anneal of 800°C for 1 h is necessary for full removal of the implantation damage [16] At the end of range ions implanted into $LiNbO_3$ have been shown [8, 15] to decrease the index of refraction by over 5 percent Reducing the host index by 5 to 10 percent would result in a shift of the expected absorption peak for Ag from 520 nm to approximately 480 nm

The nonlinear refractive index of the sample after heat treatment was characterized using the Z-scan technique [15] The laser source was a tunable dye laser (with laser dye Rhodamine 6G) pumped by a frequency-doubled mode-locked Nd YAG laser (76-MHz pulse repetition rate) The tuning range was 555 to 600 nm The average power of the laser radiation applied to the sample varied from 100 to 350 mW Special attention in performing the Z-scan measurement was paid to the temporal profile and duration time of the laser pulse and also to the beam spatial profile (should be maintained Gaussian) and beam width [17, 18] Figure 3 shows the autocorrelation trace of the laser pulses used in the experiment. The trace is typical for the pulse profile between the narrowest transform limited one and the Gaussian profile [19] Half width of the autocorrelation trace (7 5 ps) gives the pulse duration (FWHM) 4 5±0.8 ps To verify the Gaussian spatial profile of the laser beam and to evaluate the beam width, we used a variable iris aperture centered with the beam Figure 4 shows experimental intensity of the beam passed through the aperture versus the aperture radius. Experimental points are well fit to the normalized transmission function $y(x)=1-\exp(-2x^2/w_b^2)$ of the aperture for the Gaussian-shaped beam with the radius (at the level $1/e^2$) $w_b = 1\ 5$ mm For the determined pulse duration time and the beam width the laser peak power density in the sample placed near the focus of the lens (125-mm focal distance) in the Z-scan experiment reaches 0 025 to 0 088 GW/cm^2

Typical Z-scan traces of the sample are presented in Fig. 5 (the closed and the open aperture scans) The closed aperture scan shows typical behavior of a nonlinear refractive medium with positive nonlinear refractive index [17] Open aperture scan shows saturation of nonlinear absorption of the sample at the distance z = 0 from the focus (optical transmission peak in Fig. 5, bottom line) The measured nonlinear refractive index of the sample is plotted against the wavelength in Fig 6 (circles) It repeats the linear absorption spectrum fraction of which is depicted by a solid line 1 in Fig 6 This is a typical picture when the surface plasmon resonance contributes to the intrinsic nonlinear response of nanoclusters originated from interband, intraband, and hot electron photo excited transitions [20]

The nonlinear refractive index of the silver implanted $LiNbO_3$ sample was compared against Cu-implanted silica sample as a reference The sample was prepared at the conditions similar to those in Ref. 4 The energy of the Cu ions and the fluence were 2 0 MeV and 1 0x10^{17} cm^{-2} respectively Implantation was performed at room temperature. Heat treatment was done at 1000°C in the air for 1 hour The nonlinear refractive index of the reference sample was characterized with the Z-scan technique at the same conditions as the Ag-implanted $LiNbO_3$ sample It is plotted together with the absorption spectrum in Fig 6 (squares and solid line 2 respectively) The nonlinear refractive index of the reference also repeats the shape of the Cu surface plasmon resonance peak in full agreement with Ref 4 The nonlinear index of the Ag-implanted sample is approximately two times greater than the index of the reference. The optical density is greater as well At the same time, the fluence used to implant the silver sample is 5 times less than the fluence used for the reference We believe that this enhancement of the nonlinear refractive index and the optical density can be attributed to the high volumetric density of Ag nanoclusters in the ion-implanted layer remaining even after intensive heat treatment and possible recrystallization of the nuclear damage region in the $LiNbO_3$ matrix. The absolute values of the nonlinear index of both samples ($(8.21\pm 0.20)\times10^{-9}$ cm^2/W $\leq n_2 \leq (12.82\pm0.52)\times10^{-9}$ cm^2/W and $(4.02\pm0.30)\times10^{-9}$ cm^2/W $\leq n_2 \leq (6.82\pm0.28)\times10^{-9}$ cm^2/W for silver and copper respectively) are at least one order of magnitude greater than those for similar materials reported in the literature [4, 18]. This indicates the presence of the cumulative thermal self-focusing effect which can be still significant for short laser pulses (pulse duration time is less than 10 ps) but relatively high pulse repetition rate (76 MHz in our case versus 3.8 MHz in Ref. 4).

3. Conclusions

We have synthesized a metal nanocluster composite by implanting Ag ions in $LiNbO_3$. The composite exhibits a Kerr-type nonlinear susceptibility. The nonlinear refractive index for the Ag $LiNbO_3$ composite compares well to other metal colloid composites prepared by ion implantation. It is particularly twice as high as the index for Cu silica composite. The proposed composite can therefore be used in $LiNbO_3$-based nonlinear integrated optical devices.

4. Acknowledgments

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Figure captions

Fig 1. The concentration of the implanted Ag ions versus the depth of the $LiNbO_3$ sample calculated by the Monte-Carlo method. The energy of the Ag ions is 1.5 MeV, the fluence is 2 $0x10^{16}$ cm^{-2}

Fig 2 Optical absorption spectra of the Ag implanted $LiNbO_3$ sample The parameters of the implantation are the same as for Fig 1

Fig 3 Autocorrelation function of the pulse generated by the picosecond dye laser used for the characterization of the nonlinear refractive index of the Ag implanted sample The autocorrelation trace corresponds to the optimal length of the laser cavity The laser wavelength is 580 nm.

Fig 4 Normalized power versus radius of the variable iris aperture placed in the center of the laser beam used in the Z-scan experiment Solid line is the graph of the function $y = 1 - \exp(-2x^2 / w_b{}^2)$ which corresponds to the Gaussian profile of the laser beam with the radius (defined at the level $1/e^2$) $w_b \approx 1.5$ mm

Fig 5 Typical closed aperture and open aperture Z-scans obtained for the Ag implanted $LiNbO_3$ sample The aperture transmittance $S = 0\ 5$ (aperture radius $r_a = 1\ 5$ mm), average power is 300 mW, wavelength is 575 nm The nonlinear refractive index calculated from the Z-scan data $n_2 \approx$ 10 $12x10^{-9}$ cm^2/W

Fig 6 Nonlinear refractive index of the Ag:$LiNbO_3$ sample (circles) and Cu silica reference sample (squares) versus wavelength Solid lines 1 and 2 represent optical absorption spectra of Ag $LiNbO_3$ and Cu:silica respectively

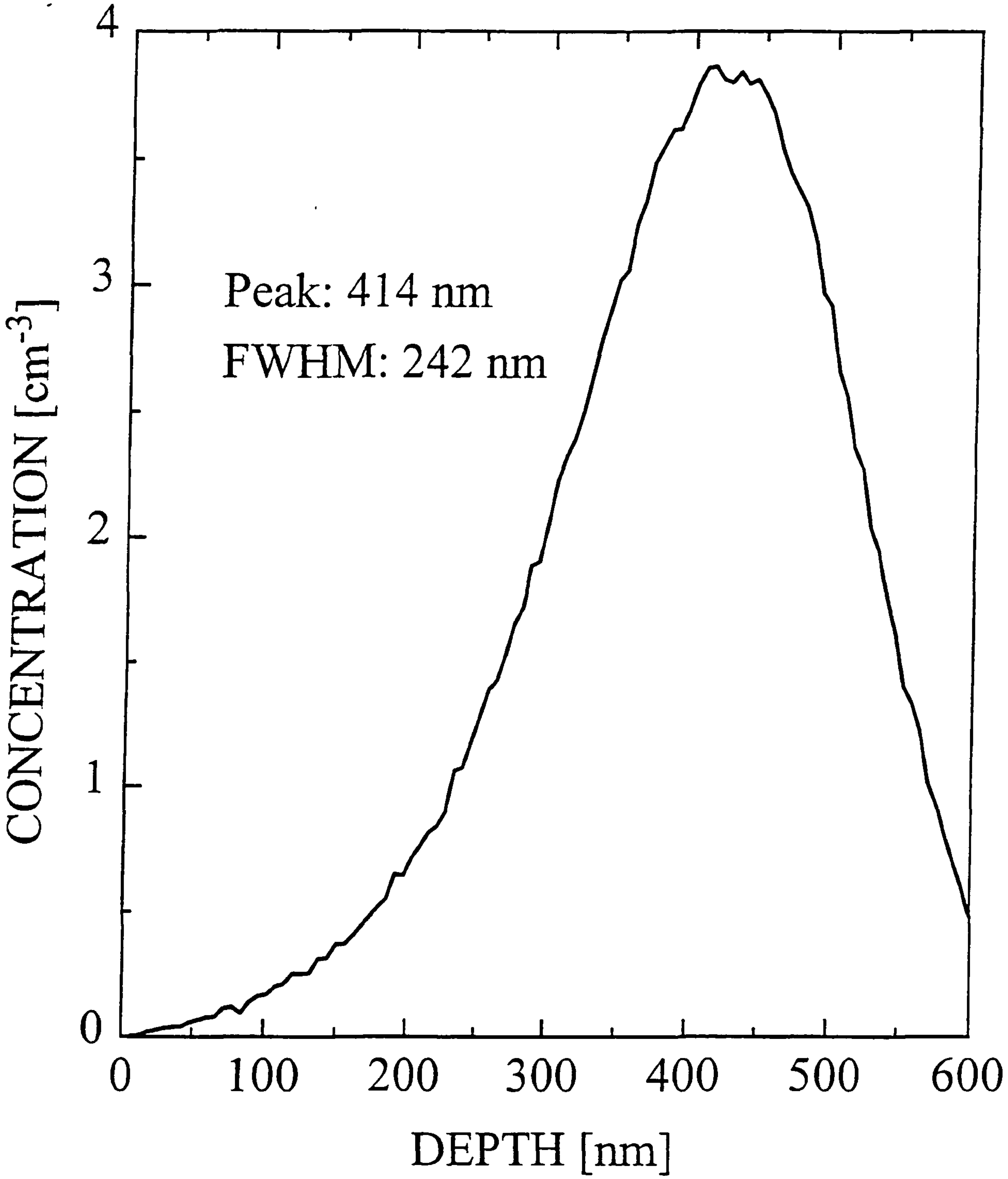

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Fig. 1

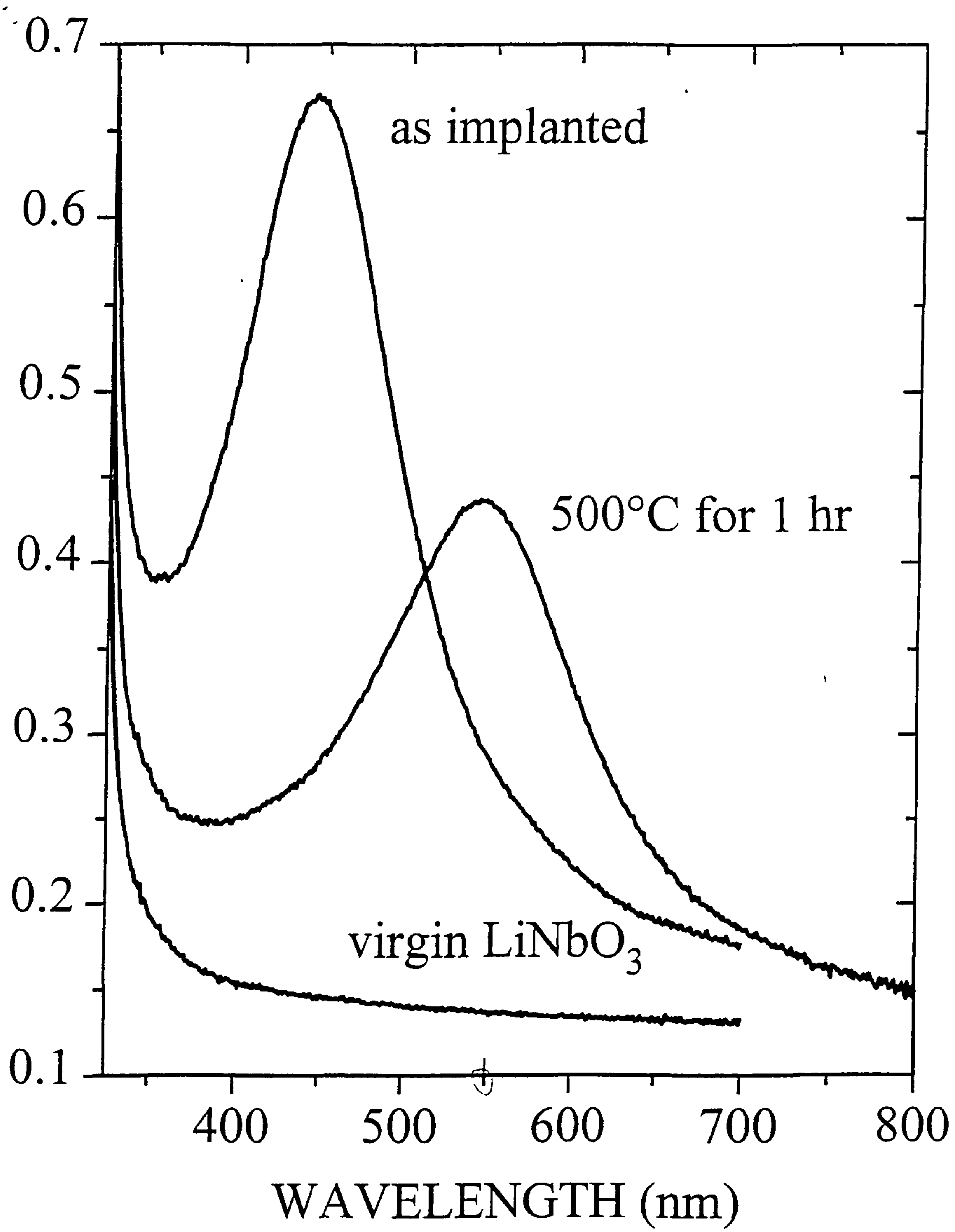

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Fig. 8

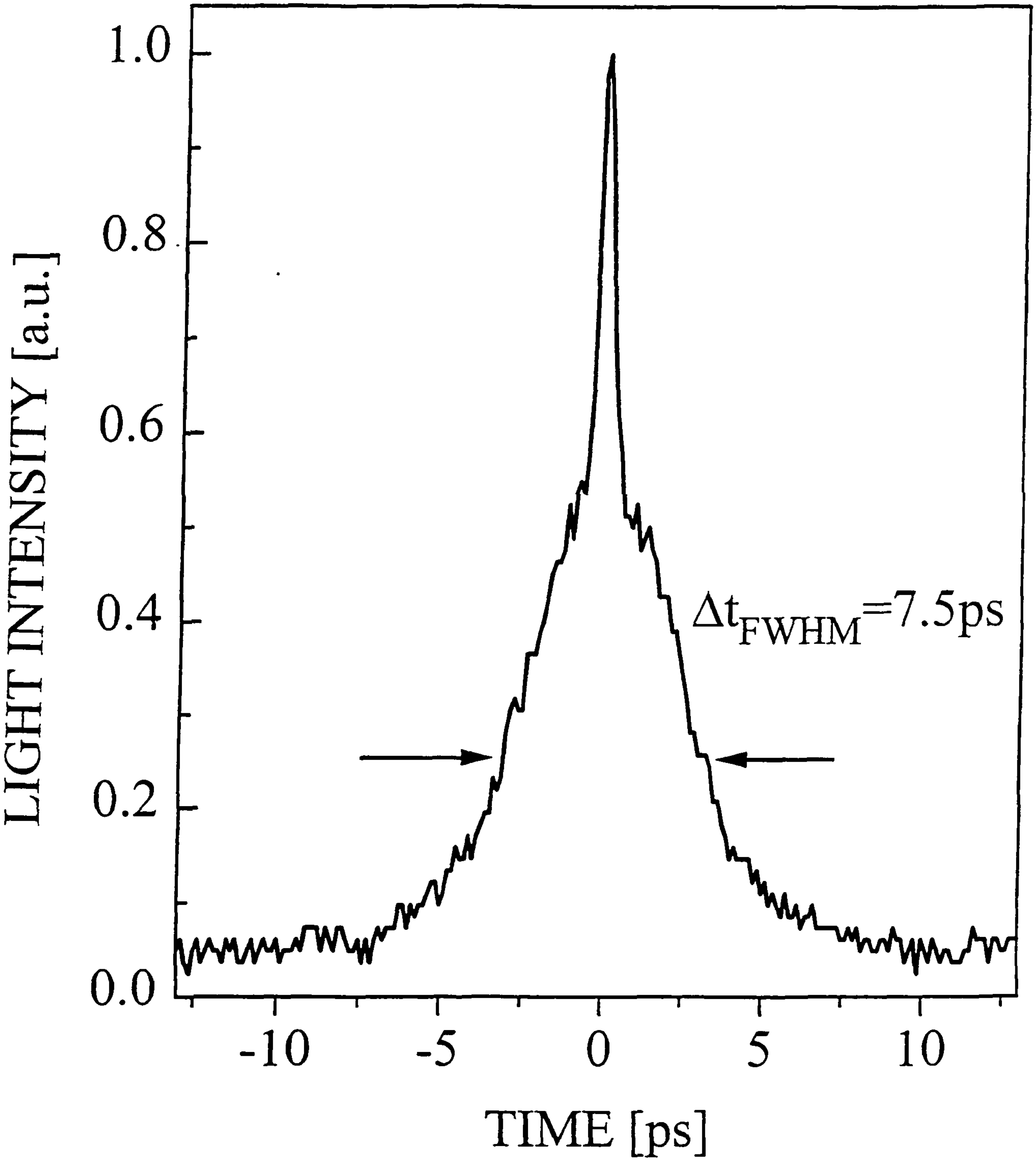

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Fig 3

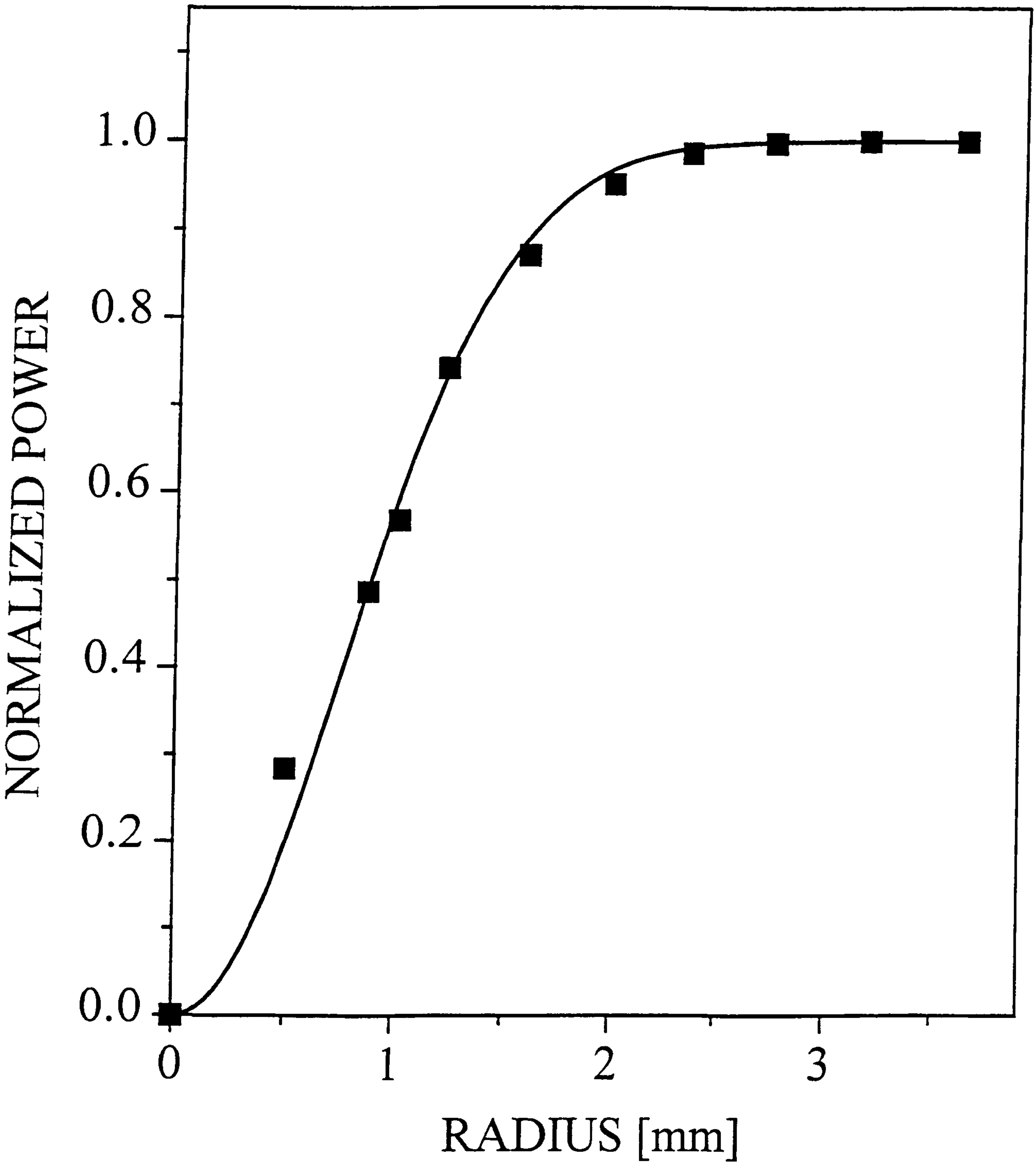

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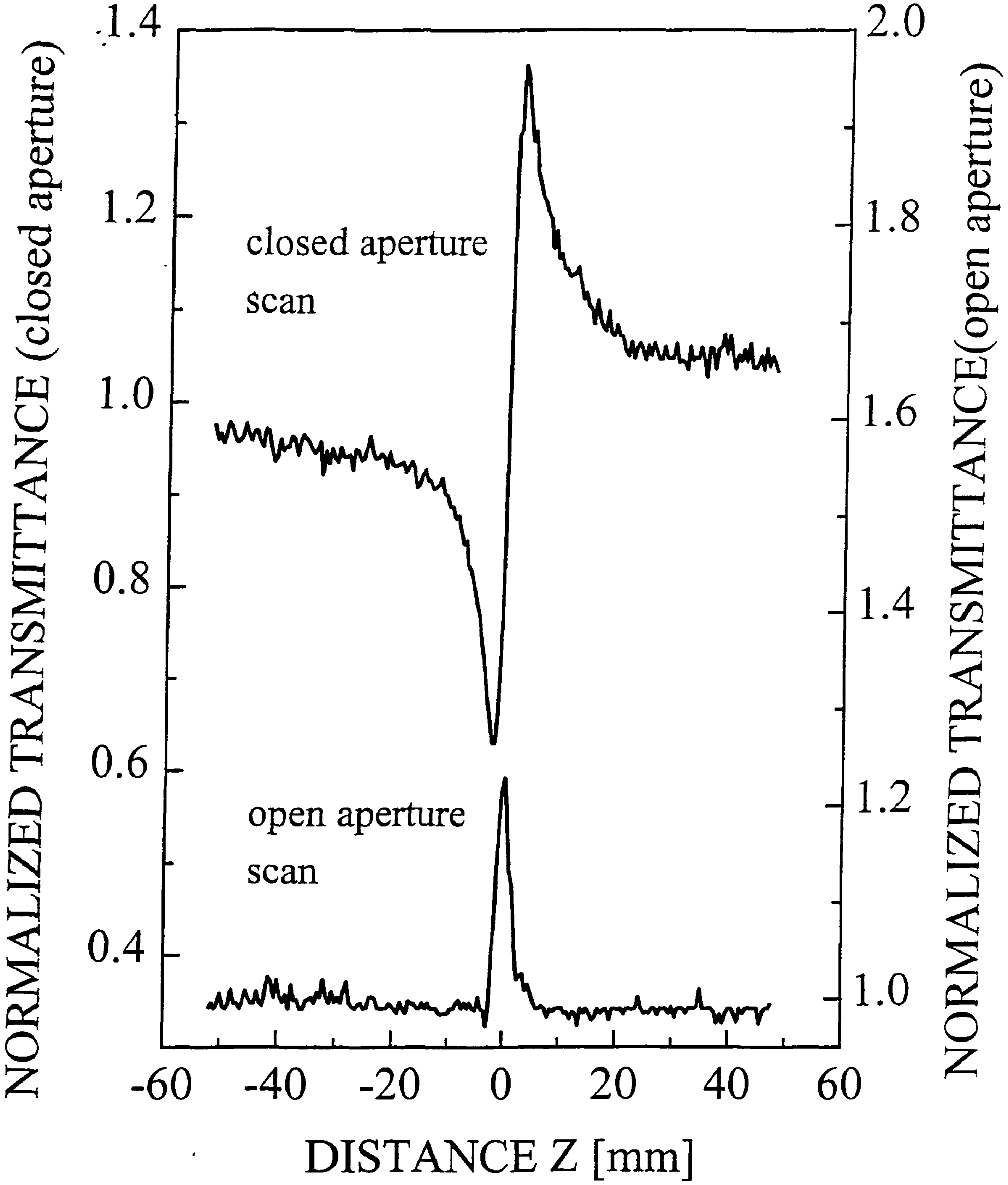
Fig. 4


NORMALIZED TRANSMITTANCE (closed aperture)
NORMALIZED TRANSMITTANCE(open aperture)
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1.2
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0.4
2.0
1.8
1.6
1.4
1.2
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closed aperture scan
open aperture scan
-60
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-20
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20
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Fig. 5

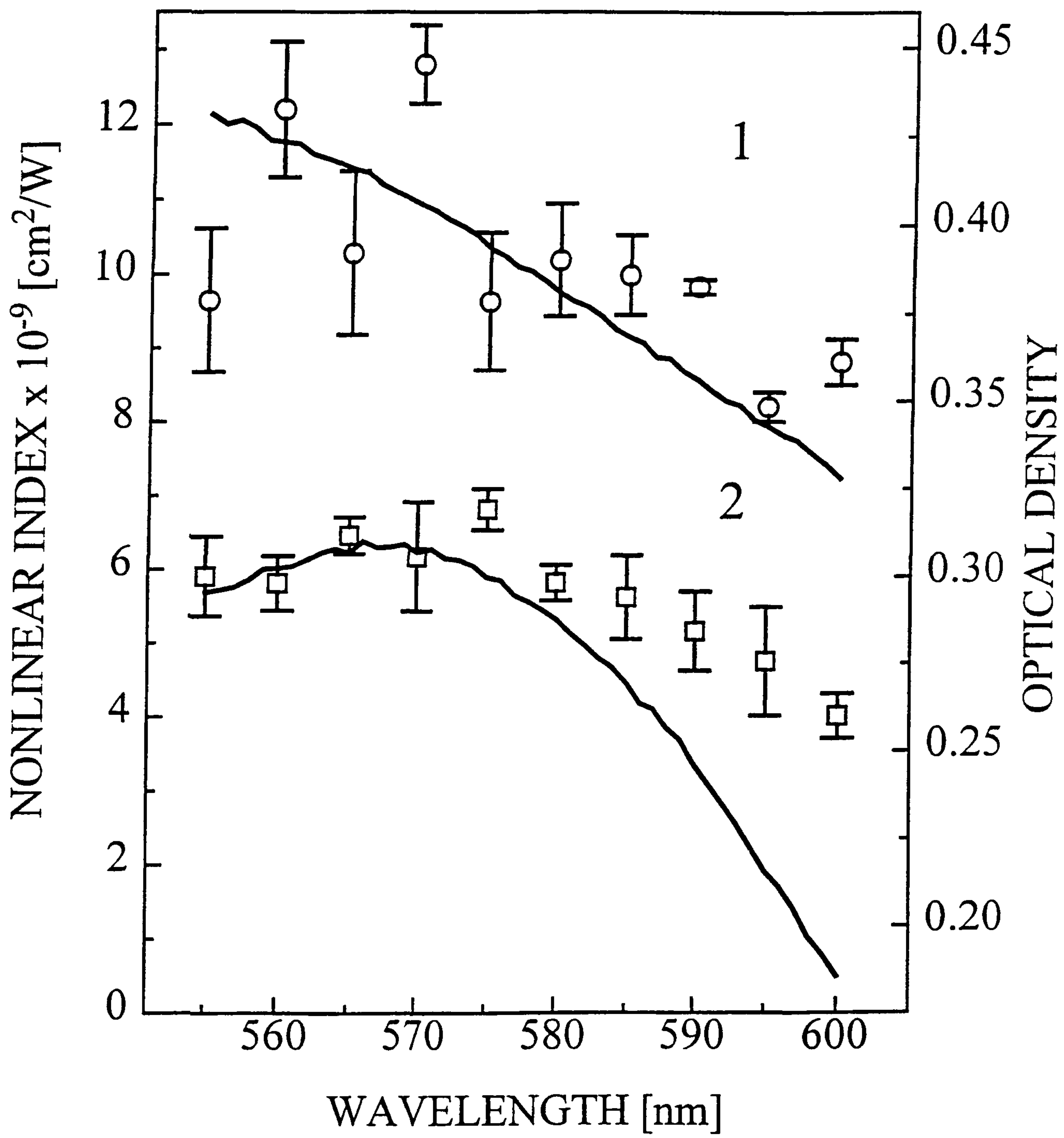

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Fig 5

DOE

⑱ DOE, XF
⑲ UC 900, DOE