REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-

0734

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	None Shown	Final

4. TITLE AND SUBTITLE
Temperature and Spectral Dependence of the Nonlinear Index of Ruby Via Nondegenerate Two Wave Mixing

5. FUNDING NUMBERS

6. AUTHORS
C. L. Adler and N. M. Lawandy

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Brown University

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NI
4040 Fairfax Dr, Suite 500
Arlington, VA 22203-1613

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
See Attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

Temperature and Spectral Dependence of the Nonlinear Index of Ruby Via Nondegenerate Two Wave Mixing

by

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Abstract

We have studied the nonlinear index of refraction of pink ruby between 565 nm and 610 nm using nondegenerate two wave mixing at 77 K and 294 K. Our new results support the model originally proposed by Venkatesan and McCall based on the large cross section of the transition from the Kramers doublets to the charge transfer band. In addition, we show that two-wave mixing can be used for accurate determination of the ^2E lifetime under conditions where radiation trapping makes fluorescence decay measurements difficult.

In 1977 Venkatasan and McCall proposed a model for the nonlinear index of ruby in the spectral region near the R-lines based on the large excited-state absorption due to the charge-transfer band ~40000 cm^{-1} above the ^2E state. They formulated this model because of the unexpected action of a bistable device at room temperature[1]. While this model is simple and appealing, there are many states above ^2E besides the charge-transfer band which could contribute to the nonlinear index. To our knowledge, there has been no thorough test of their model, although other groups have looked at the contribution of the charge-transfer state to excited-state polarizability in various different Cr^{3+}-doped materials using the lines of an Argon-ion laser.[2]

Figure 1 shows the energy levels of ruby and a number of possible states above ^2E which could contribute to the nonlinear index.[3,4,5] In the case that other states above ^2E contribute significantly to the susceptibility, their presence should produce sharp features in the spectral dependence of the nonlinear index of refraction. In addition, these narrow lines are phonon-broadened and exhibit line widths which have a strong temperature dependence, in contrast to the charge-transfer state. The experiments in this paper were undertaken to test the charge-transfer model by measuring the nonlinear index of ruby by nondegenerate two-wave mixing (NDTWM) over the spectral range 550 nm to 605 nm at 70 K and 300 K.

Two wave mixing is a process in which the interference of two waves in a medium with a third-order susceptibility induces a modulation in the index of refraction of the medium, causing energy exchange between the two beams. The effect has been used to study the resonance-enhanced nonlinear index of refraction in pink ruby since it has a lifetime appropriate for measurement by two-wave mixing techniques.[6,7]

The theory of NDTWM has been discussed extensively[6,7] For two beams propagating in a Kerr medium, $E_1 = E_s\, e^{i(\omega t - k_s r)}$, $E_2 = E_w(z) e^{i(\omega+\delta)t - kz)}$, it can be shown that for $E_s >> E_w$ (no pump depletion)

$$\frac{dI_w}{dz} = n_2' k \frac{\delta\tau}{1+(\delta\tau)^2} I_s I_w + n_2'' k \frac{1}{1+(\delta\tau)^2} I_s I_w \qquad (1)$$

where $I = EE^*$, $n_2 = n_2' + i\, n_2''$ is the intensity-dependent index of refraction, and τ is the Kerr relaxation time. In the case of a two-level system, τ is replaced by the longitudinal relaxation time of the levels involved. Equation (1) shows that peak energy exchange takes place for $\delta\tau = 1$ when the energy exchange is primarily due to the real part of the nonlinear index.

Using an Argon-ion pumped cw dye laser (running with Rhodamine 640), we determined the real part of the nonlinear index of ruby via NDTWM in the spectral region from 565 nm to 610 nm using the experimental setup shown in figure 1. A PZT, calibrated by a Michelson interferometer, was used to Doppler-shift one of the two laser beams. The PZT was driven using a triangle wave signal at 40 Hz, and the output from D2 was lock-in detected using as reference an attenuated signal from the function generator driving the PZT. Phase sensitive detection at the PZT displacement frequency insured that we only detected the two-wave mixing signal antisymmetric in the beam Doppler shift (i.e., due to the real part of n_2).

Figure 3 shows the two-wave mixing signal as a function of δ (beam doppler shift) for pink ruby (~.05% Cr doping) and dark ruby (1.8% doping) at 575 nm. The pink ruby sample was 3 mm long, with end faces cut 60° to the c-axis. The dark ruby was ~ 75 μm thick, with end faces cut 90° to the c-axis. The two-wave mixing signal for pink ruby peaks for $\delta \sim 420\ \text{sec}^{-1}$ and dark ruby at $\delta \sim 1000\ \text{sec}^{-1}$. This predicts a value of $\tau \sim 2.4$ ms for pink ruby and $\tau \sim 1$ ms for dark. These measurements agree well with the lifetime of the R-lines $\tau \sim 2.6$ ms at 300 K measured by Tolstoi and Shun'-Fu.[9] This lifetime is also in agreement with NDTWM measurements performed by Boothroyd *et al.*[7].

Estimating that NDTWM gain was ~10% of the total signal and that 200 mW from

the intense beam was focused into a diameter of 100 μm leads to an estimate of n_2~ 10^{-8}-10^{-7} cm^2/W, which is in agreement with other measurements.[6,7]

Figure 4 shows the relative value of $n_2(\lambda)$ in pink ruby from 565 nm to 610 nm determined from the two-wave mixing signal at 77 K and room temperature (~294 K). The crystal was oriented with the incident light polarized perpendicular to its c-axis. The two-wave mixing signal was normalized by dividing by the square of the laser power and by the transmittivity of our sample, which was measured on a Cary spectrometer. This made possible determination of the relative value of n_2' over the wavelength range of the dye laser.

A simple multi-level model for the origin of the resonance-enhanced nonlinear index of ruby based on its energy level structure can be constructed. We assume that all of the lines can be modelled as Lorentzians with center frequency ν_i, width γ_i, and absorption cross-section σ_i, and that the molecular system can be treated by a rate equation model. Calling the number of molecules in the ground state N_g and the number in ^2E, N_E, the real part of the susceptibility can be expressed as:

$$\chi'_{tot} = \frac{2n^2\sigma_g}{k} g_g(\nu-\nu_g)\, N_g + N_E \sum_e \frac{2n^2\sigma_e}{k} g_e(\nu-\nu_e) \qquad (2)$$

The sum is over all of the higher excited states of the system, ν_g is the linecenter of the ground state and ν_e the linecenters of the excited state absorptions, σ the absorption cross-section at linecenter of each transition, and:

$$g_i = \frac{\Delta_i}{1+\Delta_i^2}\,, \text{ where } \Delta_i = (\nu - \nu_i)/\gamma_i\,. \qquad (3)$$

For pink ruby, $\sigma_g \sim 2\times10^{-19}$ cm^2.

Letting $N = N_g + N_T$, then

$$N_g \sim N(1-\frac{I}{I_s}), \qquad N_T \sim N\frac{I}{I_s}, \tag{4}$$

assuming $^4T_2$ is essentially unpopulated due to its short lifetime, and the excited states above ^2E are essentially unpopulated. For .05% doping, $N \sim 10^{19}/cm^3$. Here $I_s = 1/B\tau$, where $B=\frac{\sigma_g}{h\nu}(\frac{1}{1+\Delta_g{}^2})$. $I_s(\Delta_g = 0) = 600$ W/cm^2.

The charge-transfer model makes several testable predictions. If there is an excited state very far detuned from the laser wavelength with a very large cross-section, then its contribution to n_2 can be expressed as:

$$n_2 = \frac{2n^2\sigma}{k}\frac{\Delta}{1+\Delta^2}\frac{1}{I_s} \sim \frac{2n^2\sigma}{k\Delta I_s} \qquad \text{for } \Delta >> 1. \tag{5}$$

Estimating the width of the charge-transfer absorption as ~2000 cm^{-1}, $\sigma \sim 10^{-17}$ cm^2, and $\Delta_e \sim 20$ [3], results in

$$n'_2 \sim 10^{-7} \text{ cm}^2/\text{W}. \tag{6}$$

This value is for linecenter of the ^4A-^4T transition. At 5145 Å the cross-section for the transition drops by almost an order of magnitude[8], leading to $n'_2 \sim 10^{-8}$ cm^2/W, in good agreement with measured values[6,7].

The real nonlinear index should follow the lineshape of the $^4T_2$ absorption, as $n_2 \sim \frac{1}{\Delta_e I_s} \sim \frac{1}{\Delta_e}(\frac{1}{1+\Delta_g{}^2})$. This explains why the sign of the nonlinear index does not change on opposite sides of the transition, as Δ_e is large and positive (~20) in the 400-600 nm region.[6,7] Another prediction of this model is that the nonlinear index should be effectively temperature independent, as the linewidth of the charge transfer state does not change significantly with temperature.[3,4,5] If the charge-transfer state is the dominant

mechanism for the nonlinear index, there should also be no sharp features in the wavelength region studied.

Our experimental observations match these predictions. The spectrum does not change from 77 K to 300 K, has no sharp spectral features, and follows the lineshape of the ^4A-^4T absorption. Contributions from other excited states would show up as noticeable temperature-dependent features in the spectrum.

This theory also explains the observed ratio of the real and imaginary parts of the nonlinear index.[6,7] Far from the excited linecenter, the frequency dependence of the imaginary part of the nonlinear susceptibility goes as:

$$\text{Im } \chi^{NL} \sim \frac{1}{1+\Delta_e^2} \sim \frac{1}{\Delta_e^2} \qquad (7)$$

Therefore, $\frac{\text{Re } \chi^{NL}}{\text{Im } \chi^{NL}} \sim \Delta_e \sim 20$, which is close to the ratio measured.[6,7] The exact value for the ratio depends sensitively on the linewidths of the three levels, and will vary with frequency, but should always be much greater than 1.

Tolstoi and Shun'-Fu note that as ruby lases on a transition to the ground state, measurement of the ^2E state lifetime through fluorescence decay is complicated by reabsorption of the fluorescence which leads to longer measured lifetimes than the true value[9]. Defining an optical diffusion coefficient, $D = \frac{1}{3\alpha^2\tau}$, for the diffusive transport of photons, the lifetime experimentally measured through fluorescence decay is given by

$$\tau^* = \frac{L^2}{2D} = 1.5(\alpha L)^2\tau \qquad (8)$$

where L is a typical sample length and α is the absorption coefficient at 693 nm. The linewidth of the R-lines decreases by a factor of 70 between room temperature and 77 K, leading to a 70 times enhancement of the absorption coefficient. At 77 K $\tau^* \sim$ 5 ms, roughly 5 times the actual value for a 1.8% doped sample with L=75 μm (the thickness of

our sample). Measurement of τ by the two wave mixing technique does not have this problem, as the appropriate length scale for NDTWM is the grating spacing in the sample as opposed to the actual sample length.

Using NDTWM we measured the lifetime of the ^2E state of our dark ruby sample from 77 K to room temperature. Figure 5 shows the lifetime as a function of temperature. Measurements on powdered samples with similar dopings by Tolstoi and Shun'-Fu are shown for comparison[9]. The lifetimes of their samples at 1.5% and 2.5% doping bracket the lifetime measured in our 1.8% doped sample.

The work done in this paper strongly supports the model for the nonlinear index of ruby based on the large excited-state polarizability due to the charge-transfer band. This model of McCall and Venkatasan is of interest because it predicts a purely real resonance-enhanced nonlinear index near linecenter which is impossible for a two-level system. We have also measured the lifetime of dense ruby as a function of temperature using two wave mixing, and found it to agree with previously measured values. This technique is therefore shown to be accurate in regimes where reabsorption makes standard fluorescence decay measurements of the lifetime difficult.

We would like to thank Ian McMichael of Rockwell International, M.S. O'Sullivan of the National Research Council of Canada, Robert Afzal at the Naval Research Laboratory, and Renee Moran of Burleigh Instruments, Inc., for several helpful conversations. We also thank Sidney Wright of Coherent Laser Systems. CLA would like to acknowledge the support of a UES Air Force Graduate Fellowship (contract F49620-86-C-0127). NML would like to acknowledge the support of NASA grant #NAG5-526, the NSF Presidential Young Investigator program, and the Alfred P. Sloan Foundation.

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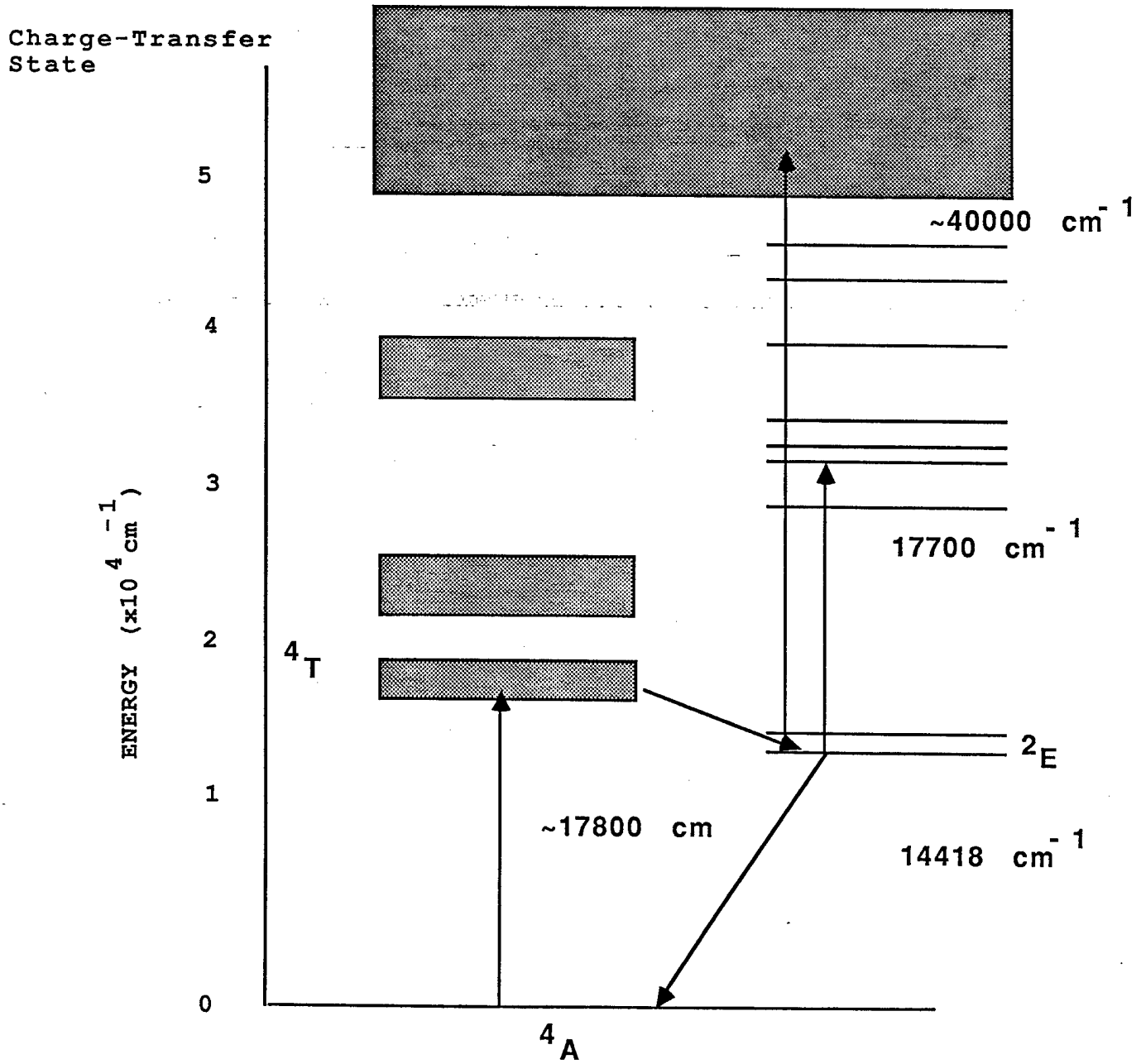

Charge-Transfer State
5
4
3
2
1
0
ENERGY (x10 4 cm -1)
~40000 cm- 1
17700 cm- 1
4T
2E
~17800 cm
14418 cm- 1
4A

fig 1

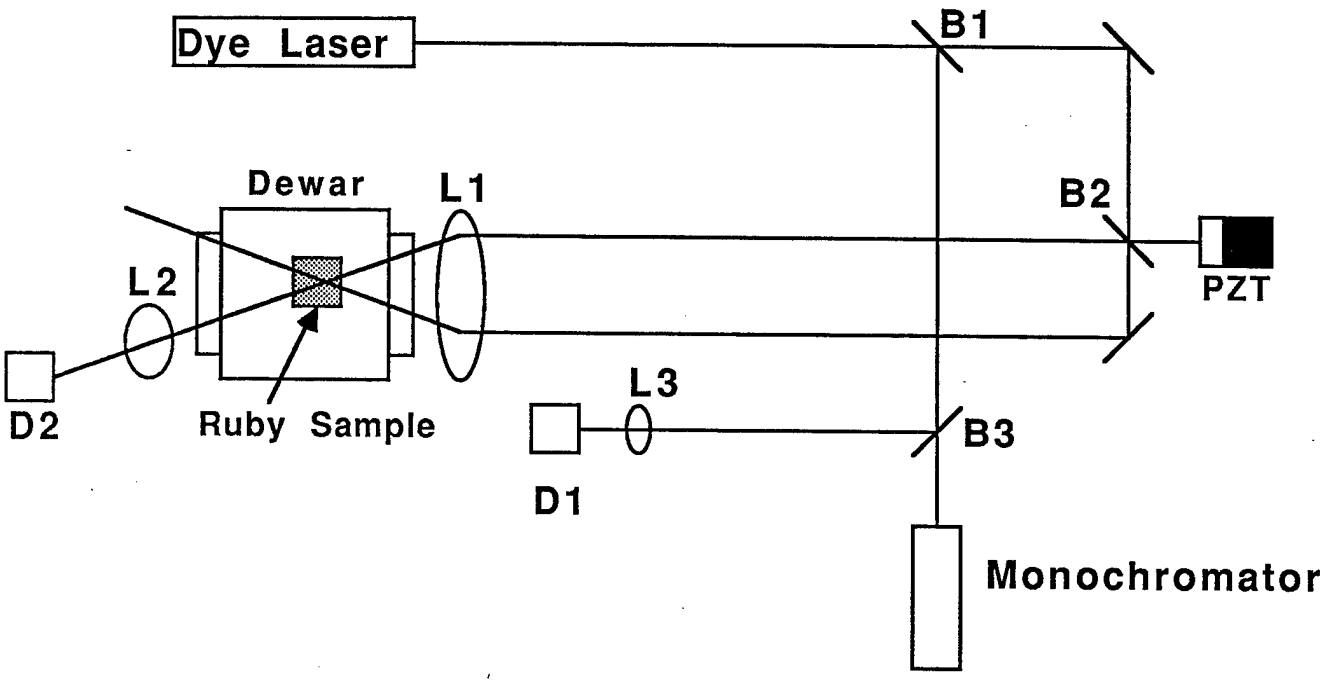
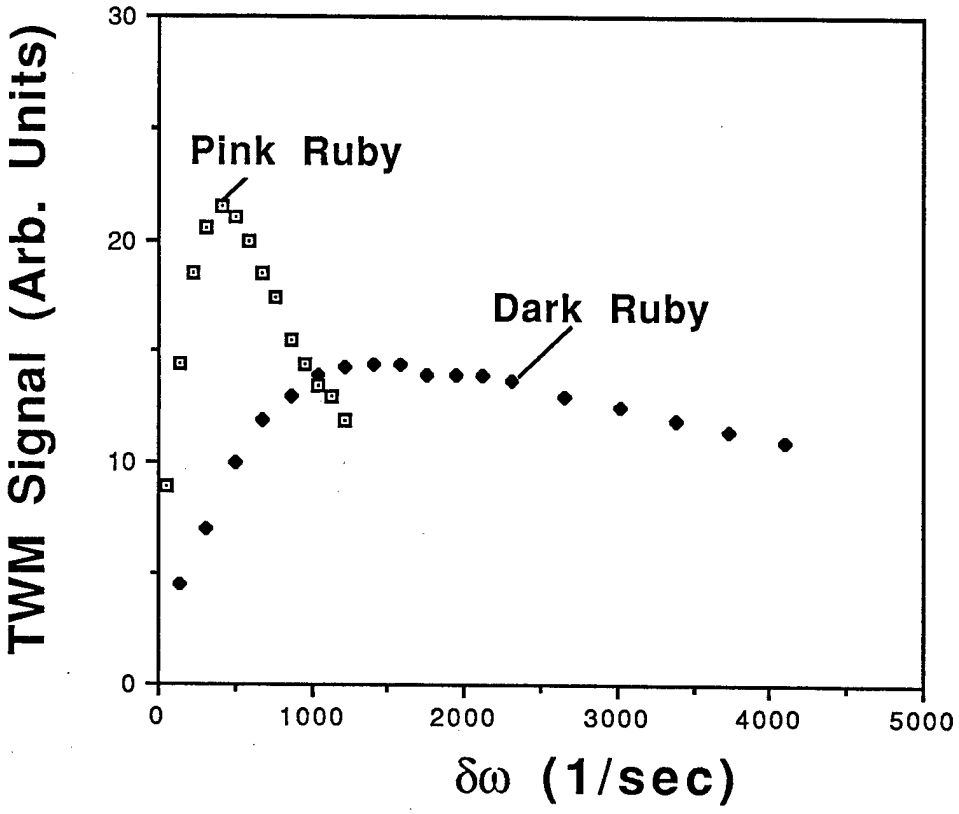
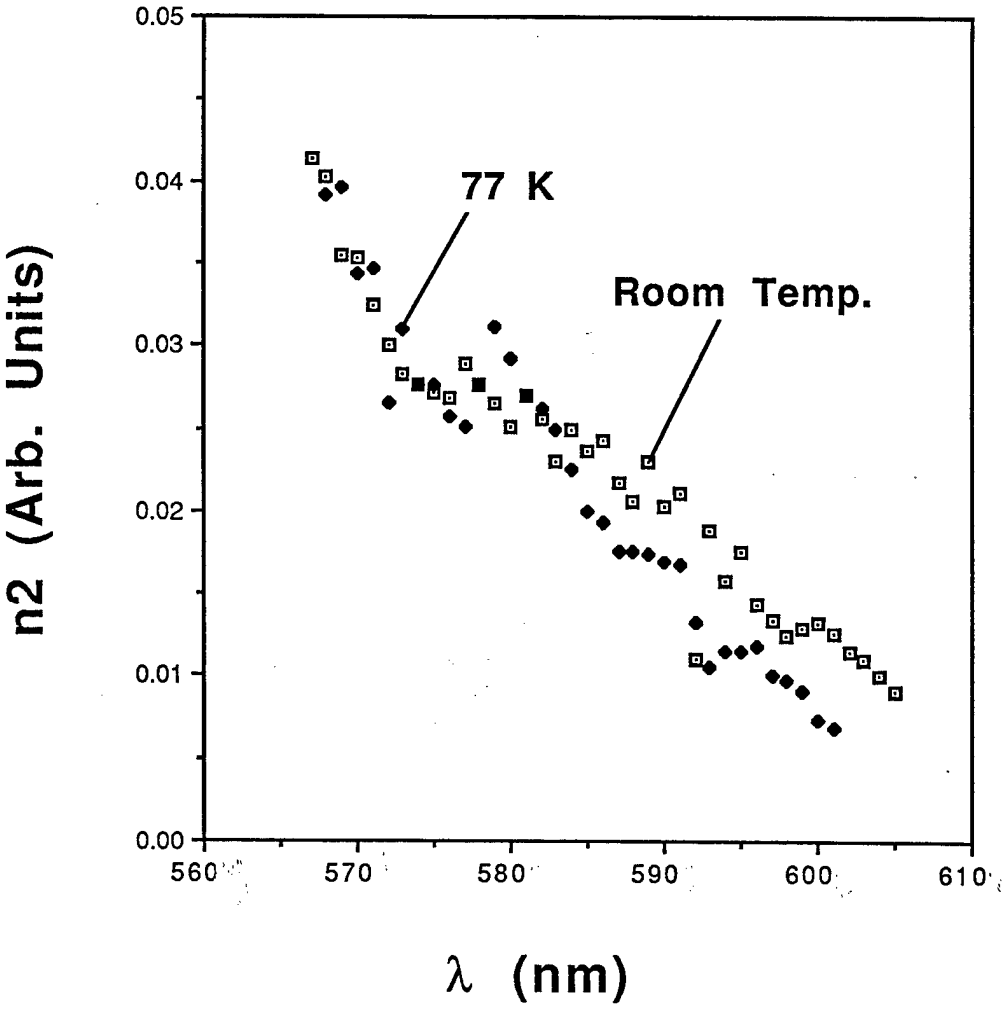
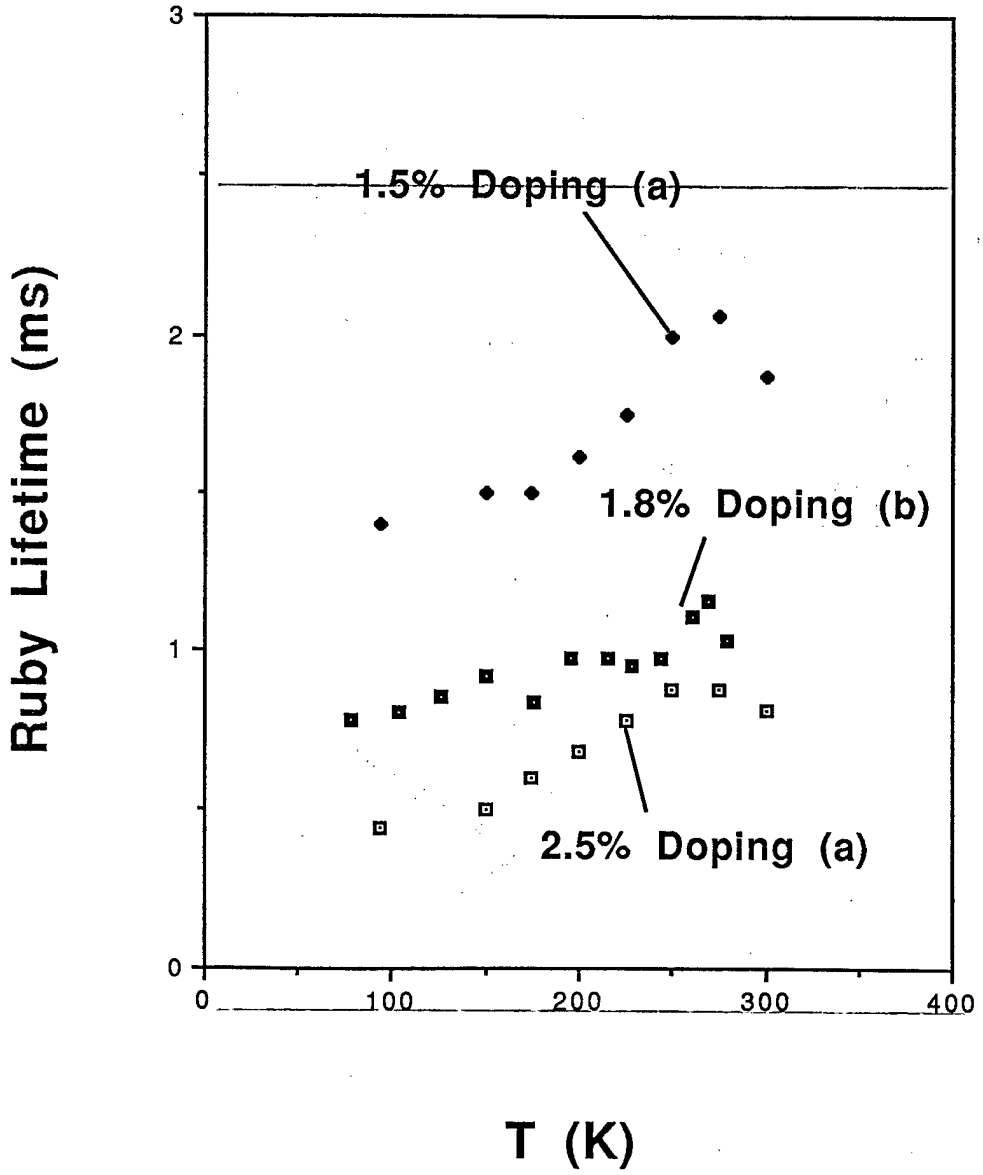

Dye Laser
B1
Dewar
L1
B2
L2
PZT
D2
Ruby Sample
L3
B3
D1
Monochromator

fig. 2


TWM Signal (Arb. Units)
30
20
10
0
Pink Ruby
Dark Ruby
0
1000
2000
3000
4000
5000
δω (1/sec)

Sig. #3


0.05
0.04
0.03
0.02
0.01
0.00
n2 (Arb. Units)
77 K
Room Temp.
560
570
580
590
600
610
λ (nm)


Ruby Lifetime (ms)
3
2
1
0
0
100
200
300
400
1.5% Doping (a)
1.8% Doping (b)
2.5% Doping (a)
T (K)

Sig 5