Absorption spectra of wide-gap semiconductors in their transparency region

Babak Imangholi *, Michael P. Hasselbeck, Mansoor Sheik-Bahae

*Optical Science and Engineering Program, Department of Physics and Astronomy, University of New Mexico,
Albuquerque, NM 87131, USA*

Abstract

The linear absorption spectra of GaP, TiO$_2$, ZnSe, and ZnS are measured in their transparency range using a two-color, excite-probe Z-scan. ZnS has the lowest absorption coefficient ($\sim 10^{-5}$ cm^{-1}) in the wavelength range 840–900 nm, making it an excellent material for use as a luminescence extracting lens in semiconductor laser cooling experiments. Direct observation of two-photon absorption in ZnSe using only low power, continuous laser beams is also reported.
© 2003 Elsevier B.V. All rights reserved.

A solid is generally considered to be transparent at wavelengths longer than its electronic absorption resonances. Absorption in the transparency spectral region can be very small, but it is not exactly zero. Reported here are measurements of absorption coefficients for materials considered to be transparent in the wavelength range $840 < \lambda < 900$ nm and having a refractive index close to GaAs ($n = 3.6$). Such substrates will be essential for efficient photoluminescence extraction in GaAs heterostructures, which is a crucial issue in laser cooling of semiconductors.

Laser cooling of semiconductors is based on a three-step process: (i) an incident photon with energy less than the mean luminescence energy is absorbed, (ii) the excitation thermalizes with the lattice through phonon absorption, and (iii) luminescence of higher energy photons occur. Anti-Stokes luminescence causes a net temperature reduction of a solid provided the up-conversion process is efficient, the luminescence can be efficiently extracted, and negligible parasitic heating occurs in the sample or substrate. Laser cooling has been observed in rare-earth doped solids [1] but its realization in semiconductors has been hindered, primarily due to luminescence trapping [2].

We address the luminescence trapping problem by placing a dome lens on the surface of the GaAs

---

* Corresponding author. Tel.: +1-505-277-3301; fax: +1-505-277-1520.

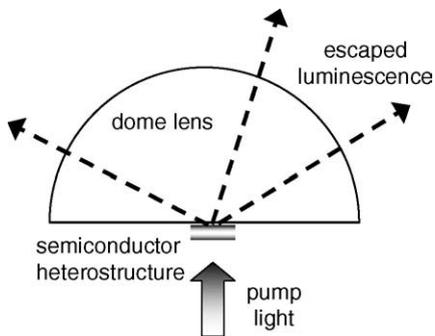*E-mail address:* babak@unm.edu (B. Imangholi).

Fig. 1. Laser cooling schematic with dome lens mounted on semiconductor heterostructure.

heterostructure (see Fig. 1). This is the usual approach in the design of efficient light-emitting diodes. The requirement for a small absorption coefficient (α) in nearly index matched lens material motivated the present work. GaAs has a nominal mean luminescence wavelength of 860 nm at 300 K. The dome lens radius is $0.5 < R < 1$ cm and the material from which it is made must have $\alpha R < 10^{-3}$ cm^{-1} [3]. We evaluate the wide-gap materials ZnS, ZnSe, TiO$_2$, and GaP in the wavelength range 840–900 nm for suitability as a dome lens. Although all candidate materials have bandgap energy much greater than GaAs, the presence of uncontrolled impurities leads to a small but measurable amount of background absorption in the near-infrared. We find that ZnSe

($\alpha \approx 8 \times 10^{-4}$ cm^{-1}) and ZnS ($\alpha \approx 6 \times 10^{-5}$ cm^{-1}) have acceptable absorption at the mean luminescence wavelength of GaAs. The refractive index of ZnS ($n = 2.4$) results in a critical angle of $\sim 45°$ at the semiconductor–lens interface and an estimated luminescence output coupling efficiency of $\sim 22\%$ [3].

There are several methods for measuring very small absorption coefficients, including cavity ring down spectroscopy [4]. Here, we use a two-color Z-scan that detects thermally induced refractive index changes with little sensitivity to background noise [5]. Since it is an opto-thermal technique, this approach is most suitable for our laser cooling application. The experimental schematic is depicted in Fig. 2. Pump light from a tunable, near-infrared cw Ti:sapphire laser (power ~ 1.5 W) is modulated with a mechanical chopper to allow lock-in detection. A thermal lens is created due to the Gaussian spatial profile of the pump and temperature-dependent index of refraction of the material. The probe beam is a low power, cw He–Ne laser (<1 mW; wavelength: 633 nm) aligned collinear with the pump beam. Pump and probe beams are focused with the same lens to spot sizes of $\omega_0 = 16 \pm 3$ and 40 ± 3 μm, respectively. Visible probe light monitors the differential refractive index change induced by the near-infrared pump laser. The sample is translated along the optical axis (i.e., the z-axis), which causes a variation of
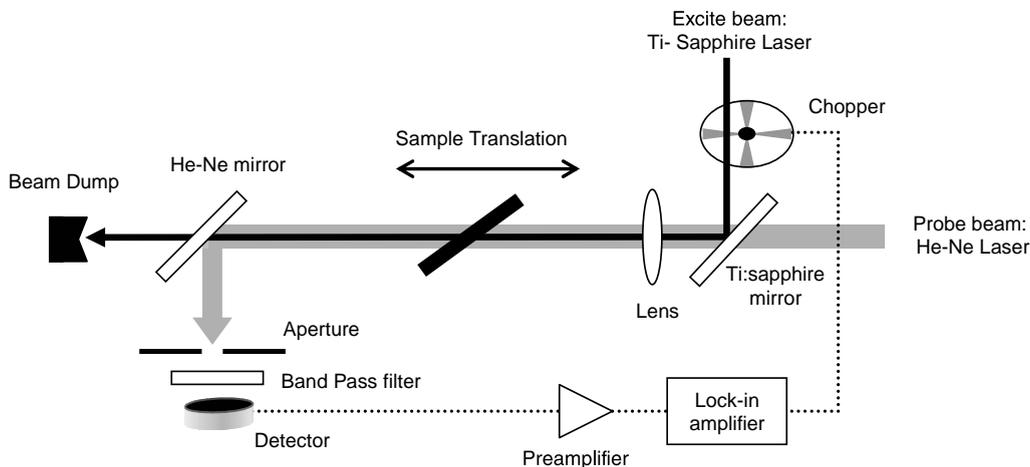

Fig. 2. Excite-probe Z-scan setup.

the pump irradiance. Changes in the probe beam divergence are monitored by a detector placed behind a partially obscuring aperture in the far-field. The size of the aperture is set for ~10% transmission of the He–Ne probe beam.

The two-color technique gives enhanced sensitivity compared to a single beam Z-scan where there can be distortion and measurement noise associated with surface imperfections. This occurs because a single laser beam encounters non-uniformities as its spatial profile changes during sample translation. Background subtraction can reduce this, but a non-ideal surface still limits the measurement accuracy. An excite-probe arrangement with lock-in detection can provide a greatly enhanced signal-to-noise ratio [5]. We are able to measure transmittance changes of <0.01% corresponding to an absorbance resolution of $\alpha L \sim 10^{-7}$ in ZnS.

Analysis of our Z-scan experiments follows [6]. We assume steady-state conditions, i.e., the time-scale of the measurement is long enough to establish a constant thermal lens in the sample. For the materials studied here, steady-state is attained in ~10^{-3} s, which is determined by monitoring the time response of the signal. This limits the maximum chopping frequency, which we keep at 30 Hz. The far-field aperture in front of the detector is set much smaller than the probe beam diameter. Under these conditions, the normalized Z-scan transmittance as a function of position (z) can be written as

$$\frac{T(z) - T_0}{T_0} = \Phi_0 \arctan \left[\frac{2m(z)v(z)}{1 + 2m(z) + v(z)^2} \right], \quad (1)$$

where the coefficient $m(z)$ denotes the ratio of probe to pump beam areas (assumed to be Gaussian profiles), $v(z)$ is a measure of the displacement of the sample from the probe beam waist, and T_0 is the transmission in the absence of pump light. The dimensionless coefficient Φ_0 depends on material parameters as follows:

$$\Phi_0 = \frac{P_{\text{excite}} \alpha L}{\kappa \lambda_{\text{probe}}} \left[\frac{\mathrm{d}n}{\mathrm{d}T} + (n-1)\frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}T} \right]. \quad (2)$$

Here P_{excite} is the excitation beam power, λ_{probe} is the probe beam wavelength, L is the sample length, κ denotes the thermal conductivity, $\mathrm{d}n/\mathrm{d}T$ is the

thermo-optic coefficient, and $(1/L)\,\mathrm{d}n/\mathrm{d}T$ represents the coefficient of thermal expansion. The linear absorption coefficient (α) is extracted in the data fitting procedure. The Gaussian beam parameters of the pump and probe light are obtained in independent measurements; they affect the shape of the Z-scan fit through the factors $m(z)$ and $v(z)$. The sample is translated ($\Delta z = \pm 3.5$ cm) through the focus of the pump beam (focal length: 15 cm).

The excite-probe experiment is calibrated using a cuvette containing a solution of 0.5% (by mass) of $CuSO_4$ in nanopure H_2O. The dilution is chosen to ensure that thermal lensing is entirely due to $CuSO_4$. We account for background absorption of H_2O and the cuvette in the data analysis. The deduced absorption coefficient of $CuSO_4$ is 0.446 cm^{-1} at $\lambda = 850$ nm, which is in excellent agreement with the value obtained in an independent measurement using an FTIR spectrometer (0.449 cm^{-1}).

Representative Z-scan data for the four materials of interest are shown in Fig. 3 at an excitation wavelength of 840 nm. The solid lines are fitted
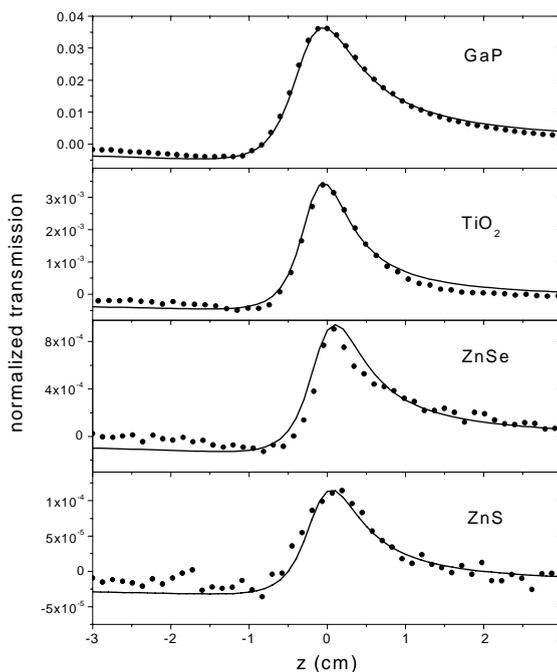

Fig. 3. Excite-probe Z-scan data at 840 nm.

curves. Reading left-to-right, all the data display a negative differential transmission followed by a peak. This is the signature of self-focusing associated with a thermally induced change to the refractive index. The dataset for GaP has a very high signal-to-noise ratio, but shows some deviation from the calculated curve at displacements far from $z = 0$. We attribute this to aberrations introduced by the pump focusing lens that prevent realization of an ideal Gaussian beam. Material parameters relevant for our analysis are shown in Table 1; this information is primarily obtained from the manufacturers. Extracted linear absorption coefficients in the wavelength range 840–900 nm are displayed in Fig. 4. TiO_2 is known to have birefringence in the near-infrared [7], but we are unable to detect changes in the response when the sample is rotated on its azimuth.

The ZnSe data are corrected for the presence of two-photon absorption (TPA). This nonlinear optical phenomenon can occur via two different physical pathways: (i) absorption of two photons from the Ti:sapphire pump laser (degenerate TPA) and/or (ii) absorption of one near-infrared photon from the Ti:sapphire laser and one visible photon from the He–Ne probe laser (non-degenerate TPA). The very low probe power of our experiment and the mode-mismatch condition make the second process negligible. Degenerate TPA, however, can become comparable to the linear absorption at sufficiently high irradiance. This can be accounted for by writing an irradiance-dependent absorption coefficient

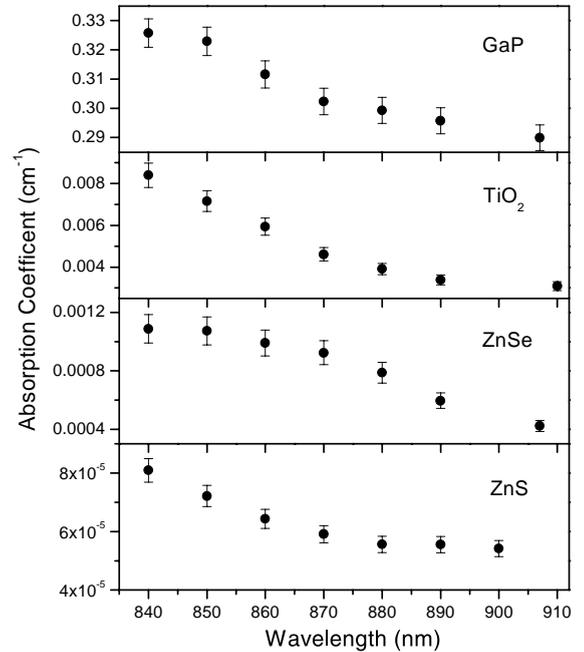$$\alpha(I_{\text{excite}}, z) = \alpha + \frac{1}{2}\beta I_{\text{excite}}(z), \tag{3}$$

Fig. 4. Linear absorption coefficients for the four materials studied.

where β is the degenerate TPA coefficient, and I_{excite} is the on-axis pump intensity at a given position (z). A geometric factor of 1/2 accounts for a spatially averaged Gaussian pump beam. We separate linear from nonlinear absorption using the following procedure: The sample is translated to the position of maximum differential probe transmission (i.e., the point of peak signal). The pump irradiance is then varied to generate the data shown in Fig. 5. Deviations from a linear response (solid line) indicate the presence of degenerate

Table 1
Material parameters used in the analysis

	E_g (eV)	n	κ (W/(cm deg))	C_p (J/(cm³ deg))	D (cm²/s)	dn/dT (deg⁻¹)	$(1/L)(dL/dT)$ (deg⁻¹)
ZnS	3.8	2.4	0.19	1.91	0.099	6.4×10^{-5}	6.497×10^{-6}
ZnSe	2.67	2.46	0.16	1.79	0.089	1.06×10^{-4}	7.57×10^{-6}
TiO_2	3.65	2.9	0.11	3.05	0.036	-5.7×10^{-7}	8.17×10^{-6}
GaP	2.25	3.3	1.1	1.78	0.62	3.3×10^{-4}	4.65×10^{-6}
H_2O	–	–	0.6	4.2	0.14	-8×10^{-5}	–

Samples were acquired from Lambda Precision Optics, Costa Mesa, CA (ZnS, ZnSe); Crystallod, Somerville, NJ (TiO_2); MTI, Richmond, CA (GaP).
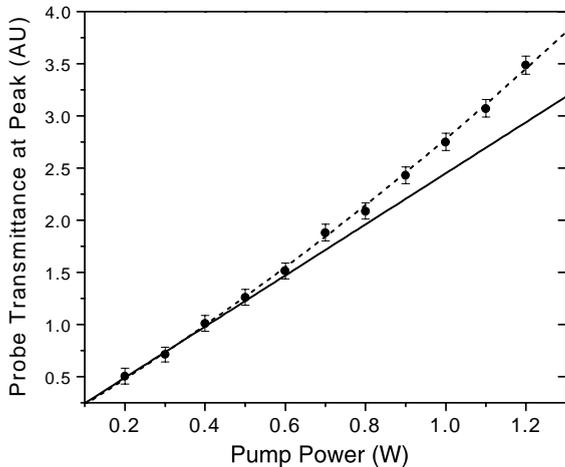
Fig. 5. Nonlinear thermal refraction obtained with ZnSe. Dotted line represents model fitting including degenerate two-photon absorption of pump photons. Solid line is a linear extrapolation of the low irradiance data.

TPA. When the far-field aperture is removed, the Z-scan signal will reveal only nonlinear absorption. This so-called open aperture data are then subtracted from data taken with a partially transmitting aperture to extract the thermal-refraction signal. The Z-scan data shown in Fig. 3 are corrected for nonlinear absorption in this way.

Two-photon absorption is a third-order nonlinear optical process; observation of this effect normally requires large optical electric fields associated with pulsed, high irradiance laser beams. Detection of TPA with only cw beams is an indication of the high sensitivity of our excite-probe technique. The dotted line in Fig. 5 represents a calculation that includes both linear absorption and degenerate TPA. We fit the data using a TPA coefficient of $\beta = 3.2$ cm/GW. A value of 3.5 cm/GW was obtained previously at $\lambda = 780$ nm by using high power, ultrashort laser pulses [8]. A calculation based on a 3-band model of a semiconductor (light- and heavy-hole valence bands and a conduction band) yields 2.1 and 3.95 cm/GW at wavelengths of 850 and 780 nm, respectively [9].

No evidence of TPA is seen in the other materials. TiO_2 and ZnS are not two-photon resonant at Ti:sapphire laser wavelengths. The large background absorption prevents observation of TPA in

GaP. The first report of TPA using cw lasers was an indirect measurement involving the magneto-photoconductivity of InSb [10]. Here, we make what we believe is the first direct observation of nonlinear transmission of a cw laser beam induced by TPA.

In summary, we have used a sensitive, two-color Z-scan technique to measure the absorption coefficients of ZnS, ZnSe, TiO_2, and GaP in their transparency wavelength range between 840 and 900 nm. We attribute this background linear absorption to transitions involving the Urbach tail and the presence of uncontrolled impurities. It is found that ZnS has the lowest absorption coefficient, which makes it suitable for use as a dome lens to remove luminescence in laser cooling experiments with GaAs. We also observe two-photon absorption with ZnSe using only cw laser beams. In this case, the nonlinear absorption can be comparable to the background linear absorption at sufficiently high irradiance.

Acknowledgements

References

[1] C.W. Hoyt, M.P. Hasselbeck, M. Sheik-Bahae, R. Epstein, S. Greenfield, J. Thiede, J. Distel, J. Valencia, J. Opt. Soc. Am. B 20 (2003) 1066.
[2] H. Gauck, T.H. Gfroerer, M.J. Renn, E.A. Cornell, K.A. Bertness, Appl. Phys. A 64 (1997) 143.
[3] M. Sheik-Bahae, R. Epstein, Phys. Rev. Lett. (submitted).
[4] A. O'Keefe, D.A.G. Deacon, Rev. Sci. Instrum. 59 (1988) 2544.
[5] A. Marcano, C. Loper, N. Melekechi, Appl. Phys. Lett. 78 (2001) 3415.
[6] A. Marcano, C. Loper, N. Melekechi, J. Opt. Soc. Am. B 19 (2002) 119.
[7] N.S. Gluck, H. Sankur, J. Heuer, J. Denatale, W.J. Gunning, J. Appl. Phys. 69 (1991) 3037.
[8] T.D. Krauss, F.W. Wise, Appl. Phys. Lett. 65 (1994) 1739.
[9] M. Sheik-Bahae, Phys. Rev. B 60 (1999) R11257.
[10] D.G. Seiler, M.W. Goodwin, M.H. Weiler, Phys. Rev. B 23 (1981) 6806.