Laser calorimetric measurement of two-photon absorption

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A laser calorimeter has been used to measure two-photon absorption in solids. This new technique provides greater sensitivity than is possible in nonlinear transmission measurements. The two-photon absorption coefficients of CdTe and CdSe at 1.06 μm using $\sim$16-nsec (FWHM) pulses are 0.13 ± 0.04 and 0.050 ± 0.014 cm/MW, respectively.

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The laser calorimeter is a device that is widely used to measure small linear absorptions at wavelengths where laser sources are available. Such an instrument can measure absorptions which are less than one part in 10^5 using a 1-W laser.[1] The calorimeter measures the total absorption due to all processes including the intensity-dependent phenomenon of two-photon absorption (TPA). Thus, the experimental technique described in this paper is based on a measurement of the total absorption as a function of the laser intensity. Calorimetric measurements of the total absorption in CdTe and CdSe as functions of 1.06-μm laser intensity were used to obtain both linear and TPA coefficients of these materials. The results can be understood by using a simple model for the attenuation with distance in the presence of TPA and by properly accounting for multiple reflections in the sample.

In 1931, M. Göppert-Mayer presented a theoretical description of TPA in which the transition probability was shown to be proportional to the square of the light intensity.[2] Thus, a material having both linear and two-photon absorption will transmit light according to the expression

$$\frac{dI}{dZ}(x,y,z,t) = -[\alpha + \beta I(x,y,z,t)]I(x,y,z,t). \qquad (1)$$

Here, $I(x,y,z,t)$ is the light intensity in MW/cm^2 and is a function of the space coordinates and time, z is the direction of propagation, α is the linear absorption coefficient in cm^{-1}, and β is the two-photon absorption coefficient in cm/MW. In many materials of interest α will be small, $\alpha \simeq 10^{-2}$ cm^{-1}, and $\beta \simeq 10^{-2}$ cm/MW according to the transmission measurements at high intensities.[3] Thus, a modest intensity of 1 MW/cm^2 will result in a two-photon contribution to the total absorption which is equal to the linear term [see Eq. (1)]. On the other hand, this intensity will result in a change in transmission for samples shorter than 1 cm of less than 1%, which is too small to be measured accurately. A comparison of the two techniques can be made by noting that in a transmission experiment one measures a small change (the reduction of transmission due to TPA) in a large quantity (transmitted intensities), whereas using calorimetry one measures a large change (the added absorption due to TPA) in a small quantity (total absorption).

The experimental procedure is to measure the total absorption as a function of intensity and evaluate the data according to Eq. (1), taking into account reflections at the rear surface. A flashlamp-pumped Q-switched, TEM_{00} mode Nd : YAG laser was the source for the experiments, as shown in Fig. 1. The laser was operated at $\sim$5 Hz with an output of $\sim$1 mJ/pulse.[4] The pulse temporal waveform was a Gaussian function with full width at $1/e$ points in intensity of 19 nsec. A beam scan was used to determine the spatial profile which was Gaussian, having a $1/e$ full width in intensity of 1.2 mm at the focusing lens. An 8-cm focal length lens was used to increase the intensity at the samples, which were placed 4 cm behind the focus. The attenuators and optics in front of the sample limited the maximum peak-on-axis intensity at the sample to $\sim$30 MW/cm^2, with an average power of approximately 5 mW. The energy per pulse was measured by averaging the output of over 100 pulses with a pyroelectric joulemeter. The accuracy of the TPA measurements is sensitive to pulse-to-pulse energy variations, which

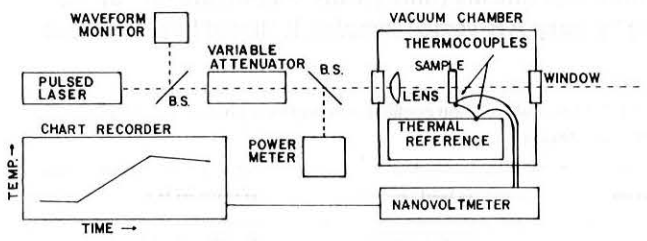

FIG. 1. Experimental apparatus for TPA measurements using laser calorimetry.

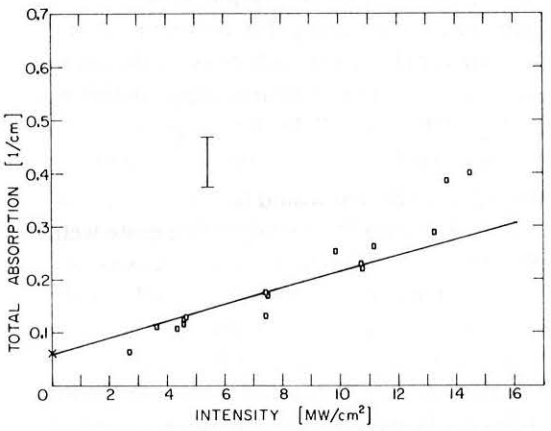

FIG. 2. Intensity-dependent absorption in CdSe: high-intensity data (□'s); low-intensity (cw) data (×); theory (–).

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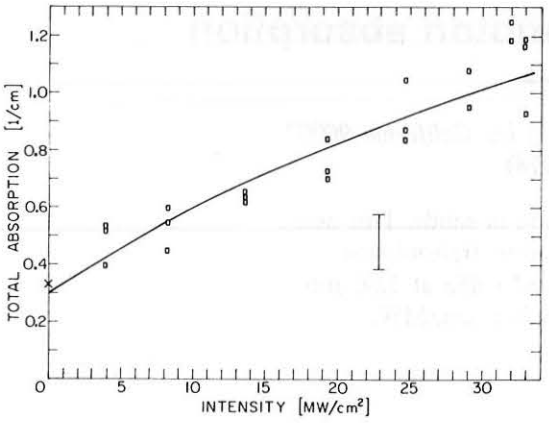

FIG. 3. Intensity-dependent absorption in CdTe: high-intensity data (□'s); low-intensity (cw) data (×); theory (–).

must therefore be kept as low as possible (~5%). The beam intensity at the sample was adjusted using a two-polarizer attenuator described in Refs. 5 and 6.

A thermocouple attached to the otherwise thermally isolated sample recorded the sample's temperature change due to the absorption of the laser light. When amplified and recorded, the thermocouple voltage appeared as shown on the chart recorder in Fig. 1. While the laser is on the temperature rises. The gentle slopes while the laser is off are due to small thermal losses that are seen with thin samples. The time constant of the calorimeter was long enough so that a 5-Hz laser beam caused no uneveness in the recorded temperature change. Thus, the calorimeter responded to the total average power absorbed. The calorimeter was of conventional design and, when evacuated, had a measured sensitivity to absorption of one part in 10^5 with a 1-W source.

Data such as in Fig. 1 was obtained at several laser intensities for room-temperature samples of CdTe and CdSe. The samples were single crystals, and the CdSe was oriented with its optic axis normal to the entrance (exit) surface. This orientation eliminated the possibility of second-harmonic generation at 0.53 μm which could be directly absorbed. The CdTe sample had its optic axis approximately 22° away from the normal to the entrance surface. Figures 2 and 3 show the intensity dependence of the total absorption of these two materials measured calorimetrically. For a small total absorption [i.e., $(\alpha+\beta I)z \ll 1$], Eq. (1) predicts a straight line for absorption versus intensity. The vertical intercept of this line gives α and its slope determines β. In these experiments which employ a Gaussian beam profile and a Gaussian temporal shape, the TPA coefficient would be $2\sqrt{2}$ times the slope in such a plot. The data fits a straight line quite well, but the total absorption at the highest intensities used for CdTe was over 20%. Thus, Eq. (1) must be solved exactly. This was done previously, including the effects of Gaussian spatial and temporal profiles, but the effects of multiple reflections were neglected.[3] For high-index materials, the intensity of the reflected beam from the rear surface can significantly affect the computed absorption coefficients. Since TPA results from the imaginary part of the third-order optical nonlinear susceptibility $\chi^{(3)}$, the field equations for both the incident and reflected beams were used to obtain the following coupled differential equations for the intensities:

$$\frac{dI}{dz} = -[\alpha+\beta(I+I_R)]I,$$

$$\frac{dI_R}{dz} = +[\alpha+\beta(I+I_R)]I_R,$$

where I is the intensity of the incoming beam and I_R is the intensity of the reflected beam. Subsequent reflections have been neglected because they contribute still less to the total absorption. Noting that the product $I(z)I_R(z)$ is a constant everywhere in the sample, these equations can be solved in closed form with the constant as a parameter. A rapidly converging numerical iterative procedure for determining the constant from the boundary conditions was used to determine the total absorption integrated over the spatial and temporal beam profiles.

The theoretical fits along with the data are shown in Figs. 2 and 3. These fits were used to obtain the values for β listed in Table I. The values given for α were obtained using a cw Nd : YAG laser and the usual calorimetric technique. These measured values of α are quite accurate and as such were used in the calculations of β. This means that the values of β given in Table I are the result of a one-parameter fit. The deviation of the fit from the data at high intensities, particularly for CdSe, may be due to a contribution from direct absorption by two-photon-created free carriers, as discussed in Refs. 3 and 7. However, at this time the data is insufficient and the error bars too large to make any conclusions concerning the possible role of free carriers. Work is continuing in this area seeking a predicted pulse width dependence to TPA if free-carrier absorption is significant.

The experimental error bars shown in Figs. 2 and 3 were determined from scatter in the data and uncertainties in determining the heating rate from curves such as sketched on the chart recorder in Fig. 1. The laser-intensity fluctuations, the accuracy of the laser-spot-size measurement, and temporal profile measurement along with the uncertainties mentioned above combine to give the quoted accuracies in Table I. The accuracy of TPA measurements using laser calorimetry has the potential for considerable improvement. The initial work presented here has, however, demonstrated the feasibility of the technique.

The inclusion of the reflected beam in the analysis of TPA measurements is essential in high-index materials, where it has been ignored previously,[3] but may be eliminated in future experiments (thus greatly simplifying the calculations) by using AR-coated samples. It should be pointed out

TABLE I. Linear absorption coefficient α and two-photon absorption coefficient β at 1.06 μm.

Material	α (cm^{-1})	β (cm/MW)
CdSe	0.062±0.06	0.050±0.014
CdTe	0.335±0.03	0.130±0.036

that in certain materials the two-photon excited level can decay through a combination of radiative and nonradiative processes. Then, part of the total TPA may not register as heat generated in the sample. This means that a simultaneous transmission measurement may make it possible to determine the quantum efficiency of such radiative transitions. This type of quantum efficiency study and measurements of TPA using two different lasers are in progress.

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