Coherent two-photon absorption spectroscopy of the Raman-active $KGd(WO_4)_2$ crystal

Arkady Major, J. Stewart Aitchison, and Peter W. E. Smith

Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Ontario M5S 3G4, Canada

Nigel Langford and Allister I. Ferguson

Department of Physics, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, UK

Received May 27, 2004

We report on the systematic open-aperture Z-scan characterization of the two-photon absorption properties in one of the most efficient solid-state Raman frequency shifters, the crystal potassium gadolinium tungstate [$KGd(WO_4)_2$]. The two-photon absorption coefficient was determined in the 370–600-nm wavelength range, with the highest value found to be ~1.9 cm/GW at 370 nm. Nonlinear losses are crucial in determining the conversion efficiency of the stimulated Raman scattering process when it is excited with ultrashort laser pulses with photon energy exceeding half of the bandgap. In addition, the results were analyzed within the context of a simple two-parabolic-band theoretical model to yield an effective bandgap energy value for the crystal. © 2004 Optical Society of America

OCIS codes: 190.4720, 190.4180, 190.5650.

Stimulated Raman scattering (SRS) is a well-established technique for frequency conversion of coherent radiation that is widely employed to extend the operating wavelength range of laser sources. Among the variety of solid-state Raman frequency shifters, the crystal of potassium gadolinium tungstate [$KGd(WO_4)_2$; KGW] is known as one of the most efficient.[1,2] Recently there has been significant interest in SRS frequency conversion of ultrashort laser pulses in the visible and ultraviolet wavelength ranges by use of KGW and other related crystals.[3–8] This activity was stimulated in part because of the short dephasing time (1.5–2.0 ps) of the vibronic Raman mode in KGW crystal.[3–5] A short dephasing time can lead to significant SRS conversion efficiencies even with ultrashort pulse pumping[3–8] despite the transient nature of the SRS process. This SRS regime occurs when the pump-pulse duration is of the order of, or shorter than, the dephasing time of the Raman mode and as a consequence is characterized by lower gain.[2,3,9]

SRS of intense ultrashort pulses in the visible and ultraviolet wavelength ranges, however, can be accompanied by a nonlinear loss such as two-photon absorption (TPA). Inasmuch as the Raman gain for ultrashort pump pulses is already reduced by the transient regime of SRS,[9] the additional effect of TPA lowers it even further and can drastically affect the SRS conversion efficiency. Note that TPA can affect not only the pump but also the generated Raman radiation, leading again to a further reduction in efficiency. Therefore characterization of the TPA properties of the Raman-active materials is critical. Unfortunately there has been no detailed study of the TPA properties of KGW crystals to our knowledge. In this Letter we report on the systematic characterization of the TPA coefficient in a KGW crystal in the 370–600-nm wavelength region by an open-aperture Z-scan technique.[10]

The laser source for the open-aperture Z-scan measurements consisted of a 1-kHz chirped-pulse amplified, picosecond Ti:sapphire laser (Titan, Quantronix) that pumped a broadly tunable optical parametric amplifier (Topas, Light Conversion) at 800 nm. For our experiments the spatially filtered output of a traveling-wave optical parametric amplifier was tuned from 370 to 600 nm with pulse durations in the 0.5–1-ps range, depending on the wavelength.

The single-beam Z-scan measurements were performed on a 1-mm-thick uncoated KGW crystal. Electric field vector E was set parallel to the N_m axis, which had Raman gain with a 901.5-cm^{-1} frequency shift.[1] The beam propagation direction was set along the N_g axis. Using a 150-mm focal-length lens, we focused the beam to a spot size of ~16- to ~30-μm diameter, which varied with wavelength. In the experiments, pulses with energies in approximately a 5–150-nJ range were used that corresponded to approximately 2–80 GW/cm^2 of the maximum on-axis pump peak intensities inside the sample. No crystal damage or Raman activity (owing to reduced Raman gain in the transient SRS regime and a thin sample) was observed in the experiments. More details of the experimental Z-scan setup can be found elsewhere.[11]

An experimental open-aperture Z-scan trace sample obtained at 500 nm is presented in Fig. 1, where normalized transmission is plotted versus distance normalized to the Rayleigh range z_0 of the beam. The data were analyzed based on a Gaussian beam optics approach that assumes that the sample is thin compared with the Rayleigh range of the laser beam,[10] which in our case varied from 1.0 to 3.8 mm. The theoretical fit is shown as a solid curve in Fig. 1 and displays close agreement with the experimental data. The estimated uncertainty of our measurements is ±25 to ±30% and is similar to those of other Z-scan measurements.[10] We determined the uncertainty of our measurements by summing all the contributing

0146-9592/04/242896-03$15.00/0

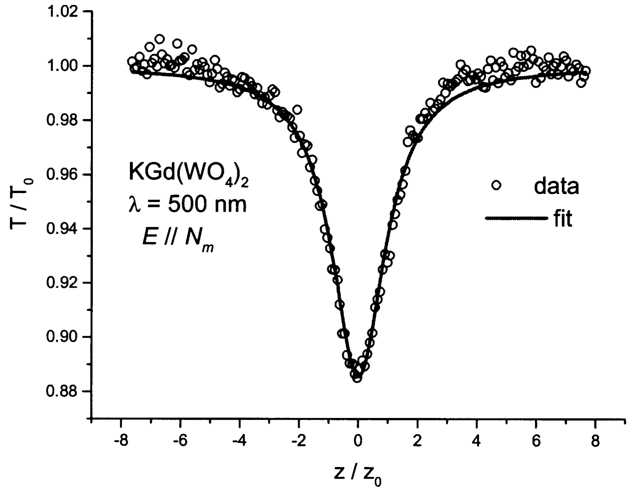

Fig. 1. Open-aperture Z-scan trace sample at 500 nm.

errors. The main contributions to the uncertainty arose from the power, the pulse width, and the beam waist radius measurements, laser power fluctuations, and uncertainties in the fitting procedure. In addition, measurements were made at several intensities to ensure that contributions from higher-order processes were negligible. Finally, we checked our results by performing control Z-scan measurements with a silica–lead SF-59 glass as a reference sample.[12]

The results of our Z-scan measurements at 370–600 nm, along with the recently reported value at 532 nm,[13] are presented in Fig. 2, where the TPA coefficient is plotted versus laser radiation wavelength for $E \| N_m$ polarization. The observed TPA increased steadily from approximately 545 nm toward shorter wavelengths, with the highest value measured to be ~1.9 cm/GW at 370 nm. At 600 nm our measurements were below the sensitivity level of our setup, which was estimated to be ~0.01 cm/GW. This observation is supported by previous measurements of the linear absorption spectrum of KGW crystals,[11,13,14] indicating the absorption edge (or cutoff wavelength λ_g) near 310–320 nm owing to the absorption lines of the Gd^{3+} ions.[14,15] Therefore TPA near 600 nm in KGW (i.e., 300-nm transition for the double photon energy) is expected to be small. We believe that the difference in the measured TPA coefficients near 532 nm in our work and in Ref. 13 can be explained mainly by the presence of SRS in the experiments of the other group (SRS has high gain for long picosecond pulses). Therefore efficient SRS at the focal point (several Stokes and anti-Stokes components were observed) can deplete the pump and effectively mimic the TPA signal.

To qualitatively explain and quantitatively support the measured wavelength dependence of the nonlinear absorption coefficient, we modeled the spectrum and scaling of the TPA in KGW crystal by using a Kramers–Krönig transformation-based model.[16] We calculated the nonlinear response by assuming only two perfectly parabolic bands with inclusion of the ac Stark and the electronic Raman effects as well as TPA. The degenerate TPA coefficient β is given by

$$\beta(\omega) = \frac{K\sqrt{E_p}}{{n_0}^2{E_g}^3} F_2\left(\frac{\hbar\omega}{E_g}\right), \qquad (1)$$

where n_0 is the linear refractive index, E_g is the bandgap energy, E_p is a Kane momentum parameter and has a value of ~21 eV, and K is a material-independent constant equal to 1940; E_g and E_p are measured in electron volts and β is in centimeters per gigawatt. The function $F_2(\hbar\omega/E_g)$ depends on the band-structure model and is a function only of the ratio of the photon energy to the energy gap of the material (or the ratio of cutoff wavelength λ_g to wavelength of interest λ).[16] One should keep in mind, however, that this simple theoretical approach, originally developed for semiconductors, provides only a general description of the spectrum and scaling in the TPA values for wide bandgap materials and therefore should be viewed as a trend guideline only. A more precise calculation would require detailed knowledge of the band structure of the KGW crystal.

The calculated TPA dispersion in KGW crystal, when we take as an estimate the previously reported E_g value of 3.97 eV (312 nm) for the N_m polarization[11] and use an appropriate Sellmeier equation[17] to take into account the dispersion of the linear refractive index, is plotted in Fig. 2 as a dashed curve. We can see that, whereas the order of magnitude of the TPA effect is predicted reasonably well, the shape of the curve is somewhat different from the observed dependence, in which no obvious TPA maximum is present. Furthermore, it can be seen that the linear absorption measurements clearly underestimate the bandgap of KGW, as no significant TPA signal was detected at wavelengths above 545 nm. The possibility of such an error in the bandgap energy estimation from the linear absorption edge measurements was mentioned earlier[16] and can be explained as being due to impurity levels, indirect gap transitions, or defects in the material.

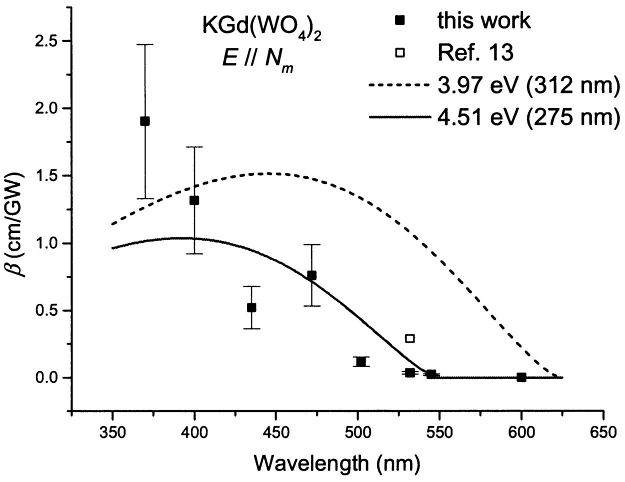

Fig. 2. Dispersion of the TPA in a KGW crystal. Error bars are set at 30%.

An alternative method for determining the bandgap energy of a material by using the measured TPA spectrum was suggested in Ref. 18. In this case the onset of TPA itself can be used as a sensitive indication of direct band-to-band transition. Following the practice of Ref. 18, we rescaled the bandgap energy in accordance with the measured TPA spectrum shown in Fig. 2 to yield an effective bandgap energy. Fitting all the data in Fig. 2 to Eq. (1) yielded a value of ~4.51 eV (or 275 nm). The fit is shown as a solid curve in Fig. 2. The recalculated theoretical TPA scaling in general gives satisfactory agreement with the measured experimental values over most of the wavelength region covered in the experiments, with some deviation at shorter wavelengths.

In conclusion, we have performed a systematic characterization of the two-photon absorption properties of one of the most efficient Raman-active crystals, potassium gadolinium tungstate [$KGd(WO_4)_2$]. We used the open-aperture Z-scan technique to obtain spectral information about the scaling of the TPA coefficient in KGW in the 370–600-nm wavelength range, which is crucial for determining the overall conversion efficiency in steady-state and especially in lower gain transient SRS regimes. The highest value of the TPA coefficient was determined to be ~1.9 cm/GW at 370 nm. The spectrum of TPA was also analyzed by use of a simple Kramers–Krönig transformation-based model and yielded an effective KGW bandgap energy value of 4.51 eV (275 nm) for high Raman gain N_m polarization with a frequency shift of 901 cm^{-1}.

The authors acknowledge the technical assistance of V. Sukhovatkin with the experiments and the help of I. Nikolakakos with theoretical data fitting. This research was supported by the Natural Sciences and Engineering Research Council, Canada. A. Major's e-mail address is a.major@utoronto.ca.

References

1. I. V. Mochalov, Opt. Eng. **36,** 1660 (1997).
2. P. G. Zverev, T. T. Basiev, and A. M. Prokhorov, Opt. Mater. **11,** 335 (1999).
3. P. Černý, P. G. Zverec, H. Jelínková, and T. T. Basiev, Opt. Commun. **177,** 397 (2000).
4. A. S. Grabtchikov, R. V. Chulkov, V. A. Orlovich, M. Schmitt, R. Maksimenko, and W. Kiefer, Opt. Lett. **28,** 926 (2003).
5. J. Findeisen, H. J. Eichler, and A. A. Kaminskii, IEEE J. Quantum Electron. **35,** 173 (1999).
6. P. Černý, H. Jelínková, T. T. Basiev, and P. G. Zverev, IEEE J. Quantum Electron. **38,** 1471 (2002).
7. L. L. Losev, J. Song, J. F. Xia, D. Strickland, and V. V. Brukhanov, Opt. Lett. **27,** 2100 (2002).
8. P. Černý and H. Jelínková, Opt. Lett. **27,** 360 (2002).
9. R. L. Carman, F. Shimizu, C. S. Wang, and N. Bloembergen, Phys. Rev. A **2,** 60 (1970).
10. M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26,** 760 (1990).
11. A. Major, I. Nikolakakos, J. S. Aitchison, A. I. Ferguson, N. Langford, and P. W. E. Smith, Appl. Phys. B **77,** 433 (2003).
12. I. P. Nikolakakos, A. Major, J. S. Aitchison, and P. W. E. Smith, "Broadband characterization of the nonlinear optical properties of common reference materials," IEEE J. Sel. Top. Quantum Electron. (to be published).
13. J. A. Dharmadhikari, A. K. Dharmadhikari, and G. R. Kumar, Appl. Phys. Lett. **83,** 2527 (2003).
14. R. Solé, V. Nikolov, X. Ruiz, Jna. Gavaldà, X. Solans, M. Aguiló, and F. Díaz, J. Cryst. Growth **169,** 600 (1996).
15. G. Aka, A. Kahn-Harari, F. Mougel, D. Vivien, F. Salin, P. Coquelin, P. Colin, D. Pelenc, and J. P. Damelet, J. Opt. Soc. Am. B **14,** 2238 (1997).
16. M. Sheik-Bahae, D. C. Hutchings, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **27,** 1296 (1991).
17. M. C. Pujol, M. Rico, C. Zaldo, R. Solé, V. Nikolov, X. Solans, M. Aguiló, and F. Díaz, Appl. Phys. B **68,** 187 (1999).
18. R. DeSalvo, A. A. Said, D. J. Hagan, E. W. Van Stryland, and M. Sheik-Bahae, IEEE J. Quantum Electron. **32,** 1324 (1996).