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Specific features of the telluride glasses doped by Pr^{3+} nanocrystallites

J. Wasylak [a], I.V. Kityk [b,*]

[a] *AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Glass and Ceramics, Mickiewicz ave. 30, 30-059 Kraków, Poland*
[b] *Institute of Physics, J. Dlugosz University of Czestochowa, Al. Armii Krajowej 13/15, Czestochowa, Poland*

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Abstract

Photoinduced two-photon absorption (TPA) measurements of Pr^{3+}-doped Te glasses under illumination of excimer Xe–F laser ($\lambda = 221$ nm) (as a source of the photoinducing pumping beam) was performed. The pumping beam formed a thin surface layer in which photoinduced TPA was observed. The Raman shifted Nd–YAG laser radiation ($\lambda = 2.9$ μm) as well as its second and fourth harmonics ($\lambda = 1450$ and 725 nm, respectively) were used as probing beams. The highest values of the TPA β-coefficient were obtained for the parallel polarizations between the pumping and probing beams. The obtained values of TPA coefficients indicate a possibility of using Pr^{3+}-doped nanocrystals incorporated into glasses as optically-operated limiters in the wide spectral range. Higher output TPA was achieved for collinear pump-probe light polarization. Substantial role of anharmonic electron–phonon subsystem is demonstrated.

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Keywords: Glass; Optical properties; Transition metal oxide; Preparation; Lifetime

1. Introduction

Recently an increasing interest in non-linear optical properties based on complex glasses as materials for infrared (IR) quantum electronics[1–5] has been occurred. Their wider application is restrained by the following factors:

- low values of the two-photon absorption (TPA) coefficients;
- large time response compared to crystals;
- high space non-homogeneity of the refractive indices and absorption.

A main goal of the present work consists in a search for new type of glasses with improved technological parameters. From the previous consideration,[1,2,4,5] one can expect that all of the mentioned parameters might be varied in desirable directions by synthesis of the telluride glasses doped by rare earths. The main goal of the article consists in an exploration of possibility to dope the glasses by Pr^{3+} ions forming nanocrystallites to enhance the non-linear optical two-photon absorption stimulated by external UV-laser beam of the excimer laser generating at 221 nm.

* Corresponding author. Tel.: +48 601 50 42 68; fax: +48 34 361 82 52.
E-mail address: i.kityk@ajd.czest.pl (I.V. Kityk).

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2. Experimental part

2.1. Sample preparation

All the telluride glasses doped by Pr^{3+} ions (0.2 wt.%) were synthesized in gold–platinum crucibles. High purity TeO_2, WO_3 and PbO powders were used in this investigations. The melting temperature should not be higher than 800 °C. The glasses were synthesized during 30 min, then all samples were annealed at about 370 °C and cooled at rate of about 20 K/h. The as-formed Pr^{3+} nanocrystallites possessed averaged sizes lying within 1.8–3.0 nm.

The samples were in the form of a parallelopiped 4 mm × 3 mm × 1 mm. The surfaces were polished in order to obtain surface roughness better than 0.12 μm.

2.2. Non-linear optical set-up

We have performed measurements of photoinduced TPA using as a source of fundamental light laser beam generation of the Raman shifted Nd–YAG laser with $\lambda = 1.9$ μm, pulse duration 22 ps, frequency repetition 11 Hz and maximal peak power about 12 MW. Simultaneously we have used the second and fourth harmonics of this laser at wavelengths 0.95 and 0.475 μm, respectively.

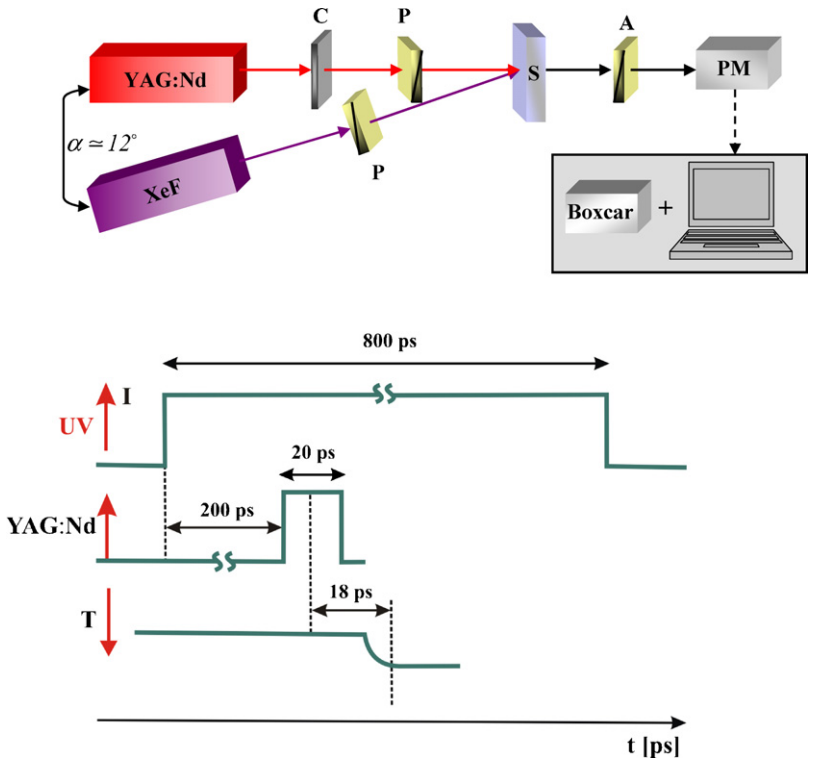

Fig. 1. Principal schema of TPA set-up.

Principal experimental set-up for performing of the photoinduced TPA measurements is shown in Fig. 1. The polarized light from the excimer laser ($\lambda = 217$ nm) creates strong electric filed polarization in thin nano-layer of the investigated glass. The system of polarizers and mirrors allows to vary the incident angle between the pumping UV-induced polarized light beam and the fundamental one within 10°–12°. The photoregistration system consisting from the photomutiplier together with the electronic boxcar registration system allows monitoring the kinetics of the output transparency versus intensity power of the probing laser beams.

Because the thickness of the UV-induced layer is equal to about 85 nm due to the glass absorption coefficient 2×10^4 cm^{-1} the effective 70–90 nm thick layer becomes a source generating anharmonic phonon modes propagating into the bulk sample and creating enhanced dipole moments determining the corresponding susceptibilities. Varying polarization of the incident and output beams we are able to analyze different geometries of optical susceptibility corresponding to the TPA.

The TPA coefficient was evaluated with precision up to 0.3 cm/GW from intensity-dependent transparency T by a method described in reference[1].

For more accurate control we have done all the measurements at different sample's thickness and at varying angles between polarizations of the pump UV light and probe IR laser beams.

3. Results and discussion

The measured dependencies of the optical transparency versus the UV-induced power density are presented in Fig. 2. One can see that at the pump power densities varying within the 0.46–0.53 GW/cm^2 substantial bending in the corresponding pump power dependences. The higher angles correspond to the higher values of the TPA. The wavelength dependences are very drastical. This one shows that the TPA dependences are spectrally dependent. Even from the qualitative consideration of the dependences one can see that there exists a drastic increase of the TPA with decreasing wavelength. A large increase of the TPA at lower wavelengths may be caused by occurrence of additional nano-confined levels, which are situated closer to the absorption edge.

Another important factor determining the possible application of the glasses consists in determination of the pump-probe response dependences. It is caused by contribution of different subsystems to the observed TPA. It is necessary to emphasize that NC are crucial for the TPA.

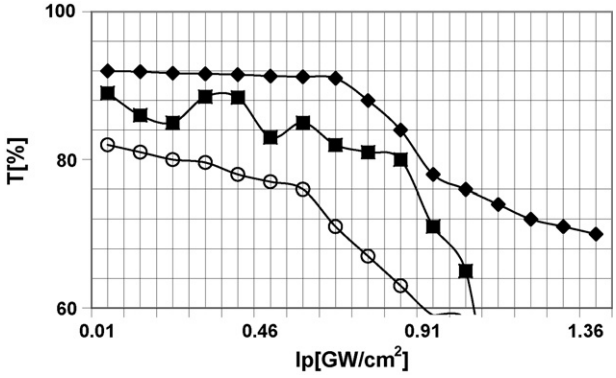

Fig. 2. Typical dependence of the intensity dependent transparency for different wavelengths: diamonds—2900 nm; squares—1450 nm; rings—725 nm.

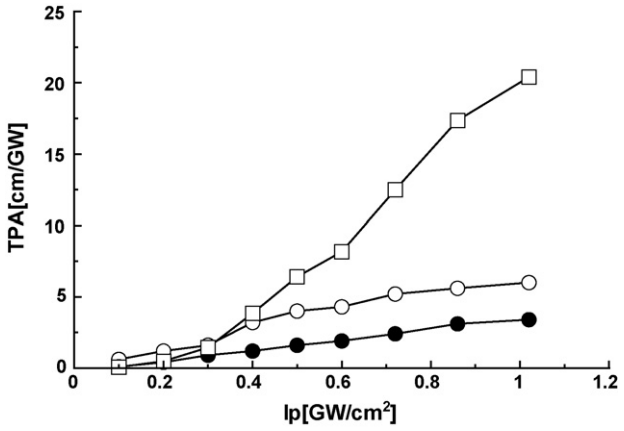

Fig. 3. Dependences of the photoinduced TPA vs. pump power density at different temperatures: (●) −196 °C; (◯) −240 °C; (□) −268.8 °C.

From Fig. 3 one can clearly see that with decreasing temperature from −196 °C down to −268.8 °C the corresponding third-order non-linear optical susceptibility described by fourth rank polar tensor substantially increases. At lower temperatures (below −243 °C) we have discovered a power saturation of the TPA.

The optimal pump-probe delaying time (which corresponded to the maximal TPA value) was equal to about 8 ps (see Fig. 4). Generally doping by Pr^{3+} ions substantially enhances the output TPA coefficient. The maximally achieved birefringence (about 0.12) was observed for a UV-induced power density equal to about 0.6 GW/cm^2. Performing cyclic cooling–heating temperature measurements, no temperature hysteresis loop was found. All the observed temperature dependencies are generally similar to that ones for another chalcogenide glasses [1–9]. However, in this particular case, the optimal pump-probe delay time is at least two times smaller. The maximal TPA signal is observed for collinear polarization of the photoinducing pumping and fundamental beams. We also have discovered that minimal light scattering losses were observed for the spot diameter of the probe laser beam equal to about 82–113 μm. All the photoinducing changes of the optical constants were reversible with accuracy

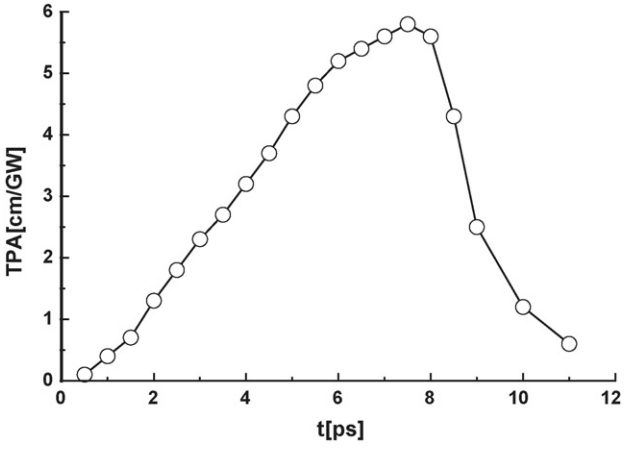

Fig. 4. Dependence of the TPA coefficients vs. pump-probe delaying times at $T = -253$ °C.

up to 0.038% (detected by phototransparency and light reflection).

All the effects were observed only during UV pump treatment and the values presented correspond to maximum of the TPA output signal after statistical averaging through the specimen's surface.

The TPA is described by fourth-rank polar tensors and is connected with photoinduced dipole transition moments. The maximal output TPA signals were observed for diagonal tensor component χ_{yyyy} where the *y*-direction corresponds to the polarization's direction of the photoinducing beam. An increase of the TPA is observed near the long- and short-wavelength edges of the transparency windows. Such unusual spectral dependence of the TPA may be related to the exhaustion of the particular virtual states and is a consequence of presence highly localized f–d rare-earth ion levels and nano-confined trapping states. Generally the value of the TPA was better compared to those for the chalcogenide glasses[1–5] without the RE doping and nano-confined effects.

From the experimental data (particularly in the picosecond regime), we have revealed a crucial role of the electron–quasi-phonon subsystem in the observed phenomena. Hence particular attention is paid to photoinduced changes of the electronic as well as quasi-phonon subsystems, which are particularly important during the photoinduced changes.

In the case of the photoinduced TPA, the non-centrosymmetry does not play a role and the values of the dipole moments and their signs become to be crucial. The latter ones determine absolute values of imaginary part of the fourth rank optical tensors directly connected with the TPA. For the TPA there exists a maximum at pump-probe delay time at about 8 ps. This minimum is caused by occupation of particular Praseodymium virtual nano-confined levels during the fourth-photon interactions. This feature is different from the three-photon interactions (case of the photoinduced optical second harmonic generation) in pure amorphous-like phase. This fact reflects also a light macro-scattering that complicates an extraction of non-linear optical susceptibilities.

So the role of the rare earth Praseodymium ions is manifested both through contribution of the highly polarized localized f–d levels as well as due to photoinduced phonon subsystem and nano-confined states. Generally the value of the effect is at least 20% higher than for the As_2Te_3–$CaCl_2$–$PbCl_2$ and Sb_2Se_3–$BaCl_2$–$PbCl_2$ glasses.[1–4] This one shows a very promising way for search of new materials for optical materials in the RE doped glasses.

During investigations of the photoinduced effects one cannot to exclude completely role played by irreversible changes.[6] Role of electron–phonon sub-systems may be changed by variation of the Praseodymium and may play very crucial role.[7,8]

4. Conclusions

We have found that the Pr^{3+} doped nanocrystallite telluride glasses demonstrate IR-photoinduced TPA substantially higher compared to similar As_2Te_3–$CaCl_2$–$PbCl_2$ and Sb_2Se_3–$BaCl_2$–$PbCl_2$ glasses without RE doping and nano-

confined quantization. With decreasing temperature (below −238 °C), a drastic enhancement of the TPA is observed. For a pump-probe delay time of about 8 ps, the output TPA signal is maximal. The optimal delaying time is at least one times smaller compared to traditional IR non-linear optical glasses, which allows to propose the glasses under investigations for the fast-respond laser spectroscopy. At the same time the specimen homogeneity is comparable to other glassy systems. We have found that the TPA increases with decreasing temperature. The obtained temperature and time kinetics dependences show on a domination of electron–phonon anharmonicity in the effects observed. The pure electronic contribution to the third-order susceptibilities was reported in reference,[9] however it cannot be used for the UV-induced operation.

All the photoinduced changes are reversible with respect to IR illumination with precision 0.010%.

Acknowledgements

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