Efficient photoinduced second-harmonic generation in Ce-doped lead germanate glasses

E. M. Dianov and D. S. Starodubov

General Physics Institute, Russian Academy of Sciences, 38 Vavilov Street, Moscow 117942, Russia

A. A. Izyneev

Institute of Radioengineering and Electronics, Russian Academy of Sciences, Vvedenskogo Square 1, Friazino, Moscow District, 141120, Russia

Received January 21, 1994

Efficient photoinduced second-harmonic generation in Ce-doped bulk lead germanate glasses is observed. A linear increase of photoinduced second-order nonlinearity with Ce concentration is obtained. The reported glasses can be encoded for frequency doubling with extremely low (as little as 30 W of peak power at 1.064 μm) preparation intensities.

Photoinduced second-harmonic generation (SHG) in glasses has attracted much attention since second-order nonlinearity is forbidden in centrosymmetric media.[1,2] However, high peak powers for photoinduced SHG in Ge-doped fibers are required, so the possible applications of this phenomenon are still limited, and more-efficient materials are expected to be developed.

It was shown that photoinduced SHG is produced by macroscopic charge separation that is due to the coherent photogalvanic effect.[3] In accordance with the proposed photogalvanic mechanism,[4] the second-order nonlinearity is induced by an electrostatic field $\mathscr{E}$:

$$\chi^{(2)} = 3\chi^{(3)}\mathscr{E}, \tag{1}$$

where $\chi^{(3)}$ is the third-order susceptibility. This field appears as a result of the charge separation by the coherent photocurrent,

$$\mathscr{E} = -j_{ph}/\sigma, \tag{2}$$

where σ is the photoconductivity and j_{ph} is the coherent photocurrent density.

To increase the photoinduced SHG efficiency it is necessary to increase the value of photoinduced second-order nonlinearity. There are two approaches to the search for appropriate materials: (1) use of materials with higher third-order susceptibility and (2) use of materials with increased coherent photocurrent density.

Studies of photoinduced SHG in bulk lead glasses have shown that the increase of third-order susceptibility with increasing lead concentration decreases the efficiency of photoinduced SHG.[5] Another possibility for increasing SHG efficiency is to increase the coherent photocurrent density. It was shown that in a Ge-doped preform the photoinduced SHG is connected with very high-order processes.[6] This is consistent with the thresholdlike dependence of the saturation level on IR preparation power and with high peak preparation intensities for grating formation. The increase of photocurrent at given preparation intensities can be achieved by a decrease of the order for the preparation process or by an increase of the concentration of photogalvanic centers (the defects that are responsible for coherent photocurrent).

In Ge-doped silica, photoinduced SHG is associated with Ge–X oxygen-deficient centers. The concentration of the defects depends on the preparation and treatment conditions. The absorption band of these defects is at ~240 nm, so the lowest-order coherent process for asymmetric photoionization—the third-order coherent photogalvanic effect—can take place only from intermediate excited states. Both the third-order coherent photogalvanic effect with population of intermediate states and higher-order coherent photogalvanic effects will result in a high-order preparation process.

The interesting alternative to Ge–X oxygen-deficient centers is ions with different valence states. The reduced form of the ion can be the donor of electrons, and the oxygenized form can serve as a trap. Efficient photoinduced SHG in Ce- and Eu-doped aluminosilicate fibers has been reported.[7] However, it is difficult to rule out the contribution of rare-earth doping, since aluminosilicate fibers without rare-earth elements produce their own photoinduced second harmonics.[8] It is more difficult to rule out the Ce contribution for photoinduced SHG in the lead-content glass GS4.[5] For elucidation of the contribution of the ions, it is necessary to use the matrices that do not produce the photoinduced second harmonic without doping.

In this Letter we report the observation of efficient SHG in Ce-doped lead germanate glasses. In our experiments a Q-switched (envelope duration ~300 ns, repetition rate ~6.3 kHz) and mode-locked (pulse duration ~600 ps) Nd:YAG laser (λ = 1064 nm) was used. Second-harmonic light was generated by a KTP crystal. The preparation radiation was focused into the sample by a 10× objective (waist diame-

0146-9592/94/130936-03$6.00/0

ter ~4.5 μm for the fundamental beam). A color filter was used to remove second-harmonic light during the reading stage. The polarization of radiation was controlled by a Glan prism. The glass sample was placed on computer-controlled positioner, which shifted the sample after each preparation.

We have studied photoinduced SHG in a pure $PbO-GeO_2$ binary system. Glasses with 10, 20, 30, 40, and 50 mol.% PbO were tested for photoinduced SHG. Each sample was studied in the interval of preparation powers up to optical damage. No photoinduced SHG was observed in all the samples, even at a long preparation time. The registration system was able to detect accurately the photoinduced SHG with conversion efficiencies of the order of $10^{-10}-10^{-11}$. The bound —Pb—O—Ge≡ in lead germanate glasses is more covalent[9] than the bound ≡Si—$O^-Pb^{2+}O^-$—Si≡ in lead silicate glasses. Therefore the absence of photoinduced SHG in pure lead germanate glasses supports the idea about the role of ionic bonds in the encoding of lead silicate glasses for frequency doubling.[5]

Next we studied glass samples with 10, 20, 30, and 40 mol.% PbO that contained 0.25 wt.% CeO_2. The IR preparation power was 500 mW, and the second-harmonic seeding power was 1 mW. The reading power was 400 mW. The glass samples with 20, 30, and 40 mol.% PbO had approximately the same photoinduced saturated second-harmonic efficiency, and the sample with 10 mol.% PbO had a significantly lower second-harmonic saturation level. The increase of PbO concentration led to a decrease of optical damage power; therefore we have chosen a $20\,PbO/80\,GeO_2$ glass system for further investigations. Recently an analogous glass was found to have potential for use in fiber lasers.[9]

The glass samples with different CeO_2 concentrations were studied. The valence of the Ce ion in glass was controlled by preparation conditions. The reading of the photoinduced second-order nonlinearity was performed by a counterpropagating IR beam for independent variation of the reading and preparation powers. The counterpropagating read IR radiation was focused into the sample by an 8× objective. The IR preparation and IR reading power was 350 mW, and the second-harmonic seed power was 1 mW. The preparation time was 3 min. The obtained dependence of the second-harmonic saturation level on the concentration of CeO_2 is shown in Fig. 1. A second-power-law approximation demonstrates the linear increase of photoinduced second-order nonlinearity with Ce concentration.

We also studied the influence of CeO_2 concentration on the erasure of induced gratings by an IR reading beam. The reading beam was blocked during the preparation. After saturation was achieved the preparation beam was blocked. Then the reading beam was launched into the sample to erase the grating. Because the relaxation time τ is inversely proportional to photoconductivity σ, it is possible to make a conclusion about the photoconductivity of the samples from $1/\tau$ dependencies (it should be noted, however, that the IR reading-beam-induced photoconductivity is not the same as for preparation conditions). The obtained dependence of $1/\tau$ on CeO_2 concentration is shown in Fig. 2. One can see that an increase in the Ce concentration by more than an order of magnitude results in a ±30% difference in relaxation time. It is possible that such a difference is caused by ununiformity of the samples. IR reading-beam intensity-dependent studies of $1/\tau$ gave an ~1.5 power law for the sample with 2 wt.% of CeO_2 in the 200–600-mW interval of reading powers.

From Figs. 1 and 2 it is possible to draw the dependence of the square root of the photoinduced second-harmonic saturation signal multiplied by σ, which is proportional to $\chi^{(3)}$ and the photocurrent density (see Fig. 3). We believe that the contribution of Ce to photoinduced SHG is connected with the creation of photogalvanic centers.

During the investigation of the samples with high concentrations of Ce, we found that the photosensitivity of these glasses is higher than the photosensitivity of lead silicate glasses and Ge-doped fiber preforms. Figure 4 demonstrates the photoinduced second-harmonic saturation level versus IR preparation power for a fiber preform with 8 mol.% GeO_2, BS7 lead silicate glass with ~50 wt.% PbO, and

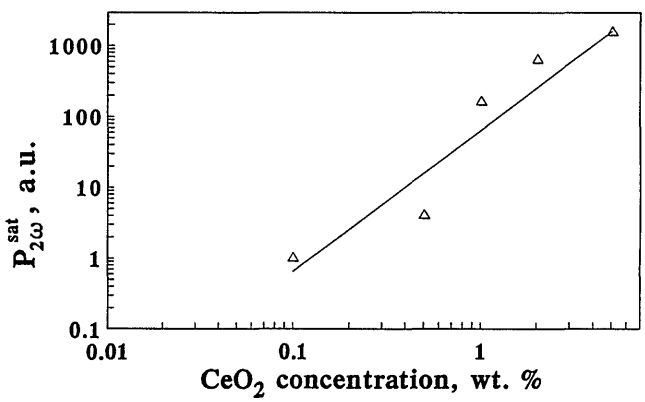

Fig. 1. Dependence of photoinduced second-harmonic saturation level on the weight concentration of CeO_2 for $20\,PbO/80\,GeO_2$ glass. A quadratic approximation is shown. IR preparation and read power is 350 mW, and the second-harmonic seed power is 1 mW.

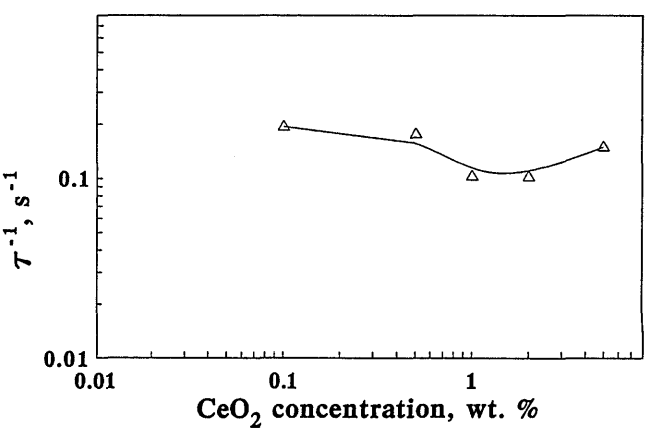

Fig. 2. Dependence of relaxation time of the photoinduced second-harmonic signal τ on the concentration of CeO_2 for $20\,PbO/80\,GeO_2$ glass. The IR read power is 350 mW.

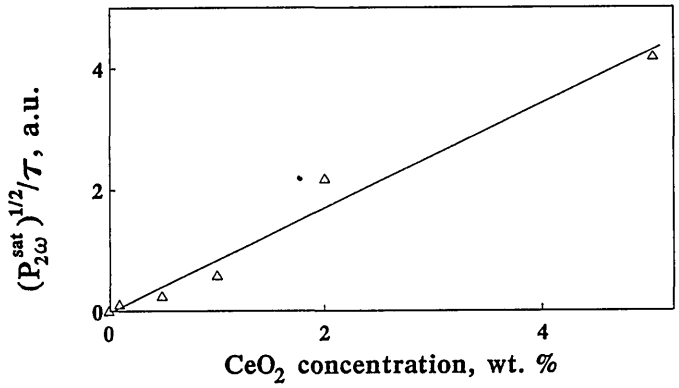

Fig. 3. Dependence of the square root of the photoinduced second-harmonic saturation signal $(P_{2\omega}^{sat})^{1/2}$, divided by relaxation time τ, on the concentration of CeO_2 for 20 PbO/80 GeO_2 glass.

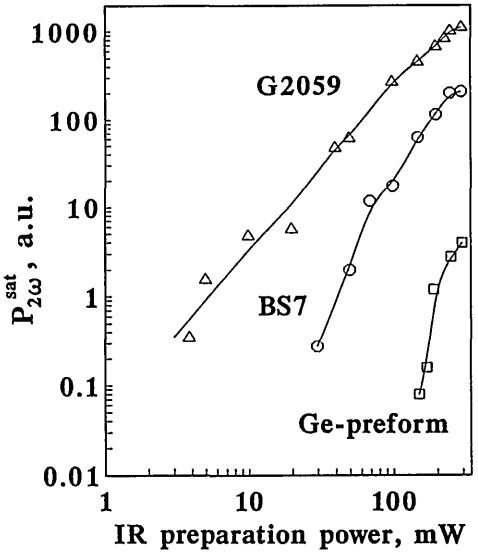

Fig. 4. IR preparation power dependencies of the second-harmonic saturation level for high-Ce-content lead germanate glass G2059, lead glass BS7, and fiber preform with 8 mol. % of GeO_2. The second-harmonic seed power is 1 mW, and the IR read power is 300 mW.

lead germanate glass G2059 with a high Ce concentration. The reading power was 300 mW, and the second-harmonic seed power was ~1 mW. One can see that the dependence for G2059 has a smaller slope. We believe that this is connected with smaller band gap of the glass. It was determined that lead germanate glasses with high Ce concentrations could be prepared with extremely low IR preparation power (as much as 30 W of peak power). The IR preparation power for these glasses is approximately 1 order of magnitude lower than for BS7 lead glass and approximately 2 orders of magnitude lower than for Ge-doped fiber preform. These properties make Ce-doped lead germanate glasses attractive for use as photosensitive material.

For elucidation of the contribution of impurities for photoinduced SHG in our samples we have examined the purity of raw components for glass preparation and the possible role of other rare-earth elements, in particular Tm, since efficient photoinduced SHG in Tm-doped fibers has been reported.[8]

The purity of raw components for our samples made it possible to suspect that the concentration of rare-earth elements is smaller than 10^{-5} of the Ce concentration. For the sample with 5 wt. % CeO_2 the upper limit of Tm concentration is 0.1–0.5 parts in 10^6 (ppm). For elucidation of the role of Tm we investigated the photoinduced SHG in Tm-doped glass without Ce and in Ce-doped glass with controlled Tm doping, in which the Tm concentration was higher than in the studied glasses. Three 20 PbO/80 GeO_2 glass samples were compared: (1) with 10 ppm of Tm_2O_3, (2) with 5 wt. % CeO_2 and 2 ppm Tm_2O_3, and (3) with 5 wt. % CeO_2. The preparation and read power was 300 mW, and the second-harmonic seed power was ~1 mW. The efficiency of photoinduced SHG in the sample doped with Tm only was more than 3 orders of magnitude lower than in the samples with Ce doping. Fast relaxation of the second-harmonic signal in the sample doped with Tm only was observed. The samples with 5 wt. % CeO_2 have shown approximately the same efficiency, apart from Tm doping.

In conclusion, we have observed efficient photoinduced second-harmonic generation in Ce-doped lead germanate glasses. A linear increase of photoinduced second-order nonlinearity with Ce concentration is obtained. The IR preparation power for lead germanate glasses with high CeO_2 concentration can be approximately 2 orders of magnitude lower than for Ge-doped fiber preforms.

References

1. U. Österberg and W. Margulis, Opt. Lett. **11,** 516 (1986).
2. R. H. Stolen and H. W. K. Tom, Opt. Lett. **12,** 720 (1987).
3. E. M. Dianov, P. G. Kazansky, D. S. Starodubov, and D. Yu. Stepanov, Sov. Lightwave Commun. **2,** 83 (1992).
4. E. M. Dianov, P. G. Kazanskii, and D. Yu. Stepanov, Sov. J. Quantum Electron. **16,** 887 (1989).
5. E. M. Dianov, P. G. Kazansky, D. S. Starodubov, D. Yu. Stepanov, and E. R. Taylor, Proc. Soc. Photo-Opt. Instrum. Eng. **2044,** 27 (1993).
6. V. Dominic and J. Feinberg, Opt. Lett. **17,** 1761 (1992).
7. D. M. Krol and J. R. Simpson, Opt. Lett. **16,** 1650 (1991).
8. D. M. Krol, D. J. DiGiovanni, W. Pleibel, and R. H. Stolen, Opt. Lett. **18,** 1220 (1993).
9. J. Wang, J. R. Lincoln, W. S. Brocklesby, R. S. Deol, C. J. Mackechnie, A. Pearson, A. C. Tropper, D. C. Hanna, and D. N. Payne, J. Appl. Phys. **73,** 8066 (1993).