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$GeSe_2$–Ga_2S_3–PbI_2 as materials for IR-stimulated optical second harmonic generation

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Abstract We have observed a several times enhancement of the IR optical second harmonic generation of $GeSe_2$–Ga_2S_3–PbI_2 glasses for the fundamental wavelength 10.6 µm. The investigations were performed after the previously treatment of the glasses by the two coherent laser beams generating by the same laser—the first one at 10.6 µm and another ones at doubled frequency (5.3 µm) obtained like a second harmonic generation signal. We have found that the maximal optical second harmonic generation was achieved during illumination by the fundamental CO_2 laser beam with power density about 1.8 GW/cm^2 , temperature about 425 °C corresponding to the glassing transitions and ratio power intensity ratio between the fundamental and doubled frequency beams about 25.

1 Introduction

Generally the second-order optical effects like second harmonic generation (SHG) are forbidden by symmetry in the randomly oriented materials including the glasses [1]. This is a consequence of an absence of inversion symmetry in the glasses. There exist different methods to favour such acentricity using external electric field (so-called electric field induced SHG) [2]. However, in the glasses transparent in the mid-infrared spectral range possessing large conductivity applying of the such fields becomes impossible. So in this case more appropriate is an application of the orientation using the two beams originating from the same light laser coherent sources and corresponding to the fundamental laser beam and its doubled frequency second harmonic generation beams. This was shown in the Ref. [3]. Afterwards a great efforts were done in the searching of new glass materials possessing enhanced non-linear optical susceptibilities [4–5]. Particular interest presents a treatment performed for the infrared materials due to IR optically stimulated anisotropy described by third rank polar tensors and favouring additional non-centrosymmetry [6–7]. It was shown also that among the glasses the more preferable are chalcogenide and chalcohalide ones [8, 9]. Following the dielectric studies of the Pb-contained glasses [10] one can expect that the Pb ions may be promising for the enhancement of the corresponding second order susceptibilities. At the same time the recent investigations performed by Kassab and co-workers have shown that the bicolour optical treatment should be maximal near the glassing temperatures [11].

As a consequence in the present work we will investigate the IR induced optical second harmonic generation for the chalcogenide $GeSe_2$–Ga_2S_3 glasses doped by PbI_2. The main goal of the investigation to achieve an enhancement of the second order susceptibility by appropriate PbI_2 doping and choosing of optimal temperature for the optical treatment.

The explanations of the observed experimental data will be done within a framework of quantum chemical and molecular dynamics simulations.

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2 Experimental

The studied glasses were synthesized by heating of the compound mixture (about 30 g) taken into the appropriate ratio. The 4N-purity Ga, Ge, S and PbI_2 up to 693 K. The process was performed in the platinum crucibles with inner diameter equal to about 5 mm during 20 h. To reduce presence of the defect, vacancies and mechanical stresses the processes a therm-oannealing procedure up to 3 h was performed at 15 K below the glassing temperature. The such process was repeated at least foures. The XRD diffraction did not show a presence of the crystallites and DSC analysis demonstrates phase homogeneity of the samples. The samples for investigations possessed the content 30 GeS_2–(50 + x)Ga_2S_3–$x$$PbI_2$. Here x was changed from 0 up to 10. The such contents were chosen following the previously performed quantum chemical simulations to achieve the largest non-linear optical coefficients. The investigated samples had the sizes about 3 × 3 × 5 mm

The optical set-up was typical for the performing of the all-optical poling (see for example Ref. [12]). The cooled PbSe detectors were used for the registration of the output PISHG.

3 Results and discussion

The measurements consists of two parts. During the first step we prepare the samples possessing the charge density non-centrosymmetry. During the next step we switch off the external fields to measure directly the output optical SHG. During the SHG measurements we have used the silica fused quartz like a reference materials.

In the Fig. 1 are presented the typical dependences of the photoinduced optical second harmonic generation (λ = 5.3 μm) versus the incident angle of the fundamental beams. The results are presented at optimal experimental conditions. These conditions were done for the angles between the fundamental and doubled frequency signals equal to about 37 °, power density of fundamental beam–about 1.8 GW/cm^2, temperature about 425 °C corresponding to the glassing transitions and ratio power intensity ratio between the fundamental and doubled frequency beams equal to about 25. The process is substantially sensitive to temperature (see Fig. 2) and the optical treatment should be durated during the several minutes (see Fig. 3). From the Fig. 1 one can clearly see that the doping by the Pb-contained compounds unambiguously enhances the corresponding output SHG. However, it is crucial that there exists an optimal concentration of the PbI_2 (equal to about 8% in weighting units) corresponding to the maximal photoinduced SHG. In our case it corresponds to the 8% of

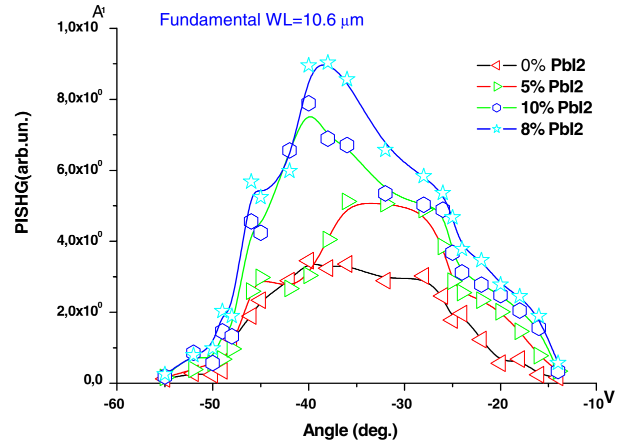

Fig. 1 Dependence of the PISHG versus the incident angle. The measurements are performed in optimal conditions as described in the text

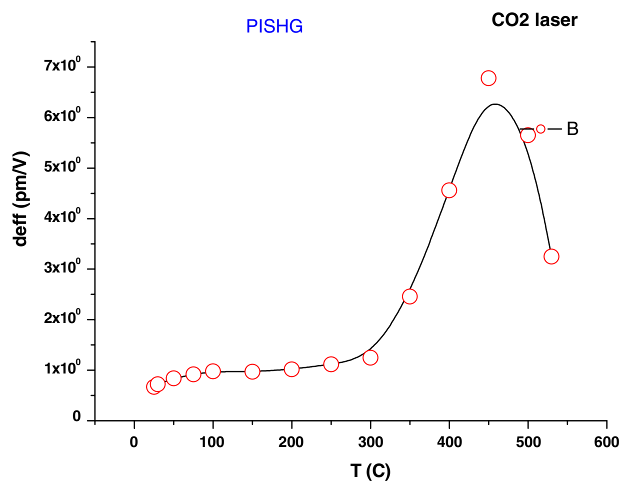

Fig. 2 Temperature dependence of the effective second order optical susceptibility for the 10% PbI2 doped samples

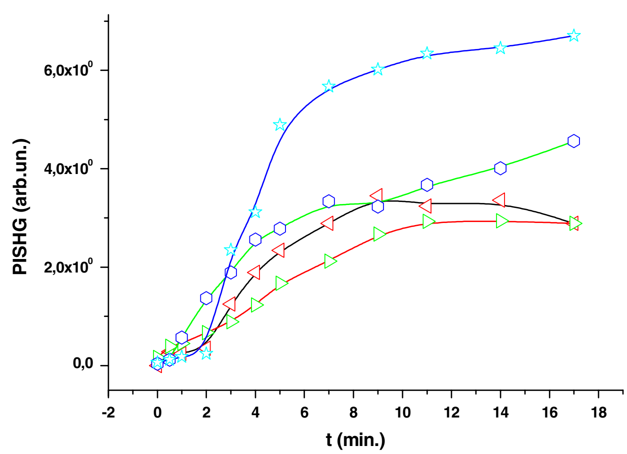

Fig. 3 Features of the PISHG during the optical coherent treatment. The indications of the samples are the same as in the Fig. 1

PbI_2. One can expect that with increasing of the Pb content the particular high polarizable Pb ions will suppress the effect. Another interesting observation consist in substantial enhancement of the PISHG near the glassing temperature equal to about 425 °C. This is in an agreement with the optical poling performed for another glasses and is caused by substantial role of the anharmonic phonons effectively participating in the processes observed.

To verify this prediction we have done molecular dynamics and quantum chemical simulation of the principal chemical clusters for the investigated glasses in the external IR induced bicolour beams. In the Fig. 4 are presented the principal clusters of the glasses before and after the optical treatment near the glassing temperature. The calculations were done by DFT method B3LYP within the HyperChem 7.5 program.The calculations are done in the applied effective electric field corresponding to the IR-induced field.

One can see that after the treatment near the glassing temperature there occurs a substantial localisation of the local electrostatic field on the principal ions. As a consequence we receive substantial enhancement of the second-order optical effects. This is indirectly confirmed by a behaviour of the photoinduced optical second harmonic generation during optical treatment (see Fig. 2). It is necessary to add that the measurements were done during the switching off of the bicolour treatment and the necessary statistics were gathered after the 150–200 laser pulses. Existence of the maxima contrary to the saturation of the process may indicate on the processes of the thermo-migration of the Pb cations in the glasses [10], which will occupy different local positions determining the second order susceptibilities.

The maximally achieved value (about 7 pm/V at 10.6 μm) for the 8% PbI_2 compounds shows a large potential of the such kinds of the glass composites like materials for the IR quantum electronics.

To show that the 10.6 μm laser plays crucial role it was performed additional treatment by the Nd-YAG laser (Fig. 5), which have shown that the changes are susbtantially lower compared to the CO_2 laser, which confirms our prediction about the crucial role of the IR laser treatment.

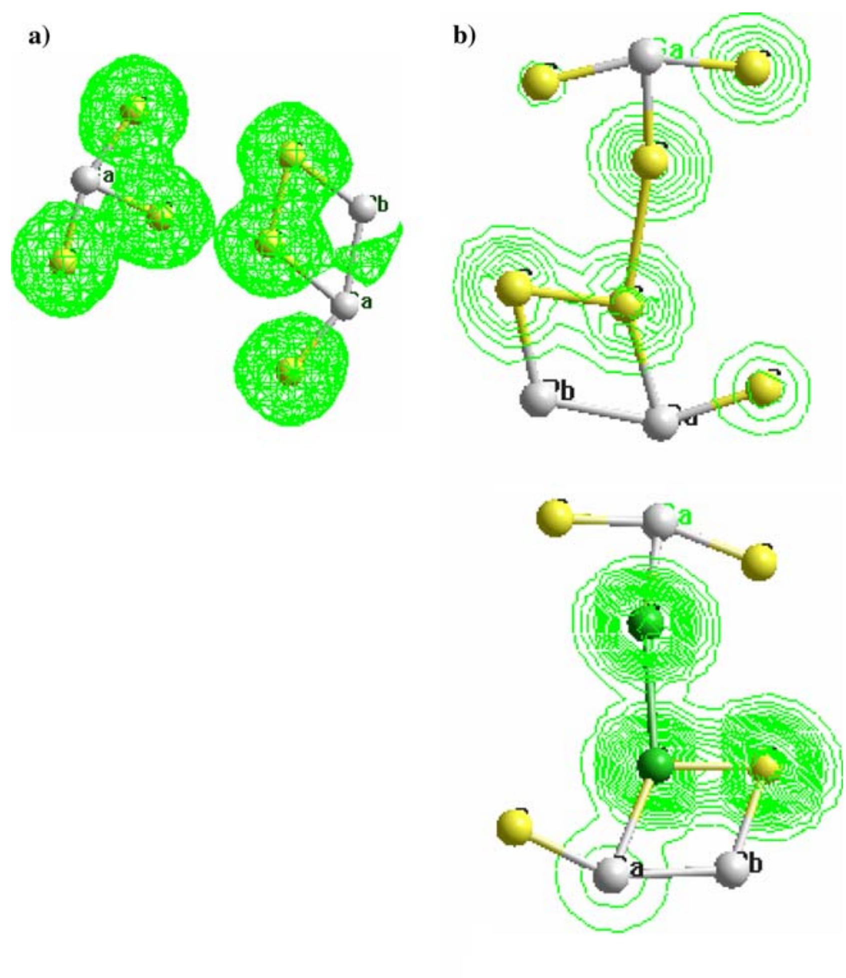

Fig. 4 Simulated changes of the principal Ge-S-Se cluster without (**a**) and in the presence (**b**) of the external IR coherent treatment

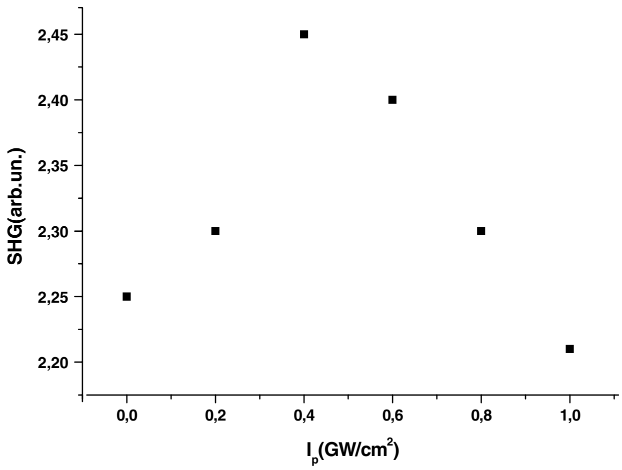

Fig. 5 Dependence of the photoinduced SHG under additional illumination by the Nd-YAG laser

4 Conclusions

During study of the $GeSe_2$–Ga_2S_3 glasses doped by the PbI_2 compounds we have established a several enhancement of the corresponding output SHG (up to 7 pm/V). There exists an optimal concentration of the PbI_2 (equal to about 8% in weighting units) corresponding to the maximal PISHG. In our case it corresponds to the 8% of PbI_2. One can expect that with increasing of the Pb content the particular high polarizable Pb ions will suppress the effect. The effect is substantially enhanced near the glassing temperature equal to about 425 °C.

References

1. A. Yariv, P. Yeh, *Optical Waves in Crystals*. (Wiley, NY, 1984), p. 506
2. J. Zyss, *Nonlinear Optics*. (Academic Press, NY, 1974), p. 254
3. U. Osterberg, W. Margulis, Opt.Lett. **11**, 516 (1986)
4. M.X. Qiu, F. Pi, G. Orriols, Appl.Phys.Lett. **73**(21), 3040 (1998)
5. M. Fokine, K. Saito, A.J. Ikusima, Appl.Phys.Lett. **V.87**, 17907 (2005)
6. I.V. Kityk, J.Phys.Chem **V. B107**, 10083 (2003)
7. I.V. Kityk, J.Modern Optics **V.51**, 1179 (2004)
8. X.F. Wang, Z.W. Wang, J.G. Yu, C.L. Liu, X.J. Zhao, Q.H. Gong, Chem.Phys.Lett. **V.399**, 230 (2004)
9. M. Guignard, V. Nazabal, J. Troles, F. Smektala, H. Zeghlache, Y. Quiquempois, A. Kudlinski, G. Martinelli, Opt.Express **V.13**(3), 789 (2005)
10. N. Krishna Mohan, K. Sambasiva Rao, Y. Gandhi and N. Veeraiah. Physica B Physica B: Condensed Matter pp. 213–226 (2007)
11. L.P.R. Kassab, R. de A.Pinto, R.A. Kobayashi, M. Piasecki, P. Bragiel, I.V. Kityk, Journ. of Phys. D: Appl.Phys. **V.40**, 126 (2007)
12. L.R.P. Kassab, W.G. Hora, M. Piasecki, P. Bragiel, I.V. Kityk, Opt. Commun (NL) **V.269**, 148–151 (2007)