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Tl_2S–Ga_2S_3–GeS_2 glasses for optically operated laser third harmonic generation

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Abstract We have shown a possibility to apply Tl_2S–Ga_2S_3–GeS_2 glasses as an effective photoinduced third harmonic generation materials. As a photoinducing beam, the 200 mW green laser at 532 nm was used. The 15 ns pulsed Nd:YAG laser with power density tuned up to 800 MW/cm^2 was used. Glass-formation region in the quasi-ternary system Tl_2S–Ga_2S_3–GeS_2 was investigated by quenching molten alloys from 1300 K. The minimum concentration of the glass-forming agent GeS_2 is 30 mol%. Characteristic thermal parameters and optical absorption spectra of the glasses of the system were investigated. The variations of the bandgap energy were determined. It is crucial that the photoinducing beam was excited in the bulk of the materials and the output third harmonic generation signal was observed for the 355 nm beam formed near the surface.

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1 Introduction

The search of suitable materials for the optically operated nonlinear optics has become an import direction in designing new optoelectronics materials [1, 2] and among them, glasses is proving to be crucial [3]. Chalcogenide semiconductor glasses composed of germanium and gallium chalcogenides are actively studied in recent years [4–9]. Their glassy alloys have broad transparency regions, are chemically stable and are promising for the use of computing devices, optical recording, and storage, nonlinear optics etc. Glass formation in the quasi-ternary systems based on the Ga_2S_3–GeS_2 side is described in many reports [e.g. 10–13]. The addition of chalcogenides of Group I elements significantly expands glass formation regions.

For instance, the Ag_2S–Ga_2S_3–GeS_2 system contains relatively large areas of glass formation at the quasi-binary sections Ga_2S_3–GeS_2 (~43 mol% GeS_2) and Ag_2S–GeS_2 (~40 mol% GeS_2) [10]. These glasses have high ionic conductivity due to the mobility of Ag^+ ions. The Li_2S–Ga_2S_3–GeS_2 system has a glass formation region at the Li_2S–GeS_2 section in the range of ~25–43 mol% Li_2S. The maximum Ga_2S_3 amount that can be added is ~23 mol%. Another glass-formation region in this system is localized at the Ga_2S_3–GeS_2 side (~90–53 mol% GeS_2), with the maximum Li_2S content about 17 mol% [11].

The addition of thallium sulfide into the Ga_2S_3–GeS_2 glasses was not previously reported. However, based on the area of the existence of glasses in the Tl_2S–GeS_2 system, quite considerable quantities are likely to be achieved.

The glass formation region in the quasi-binary system Ga_2S_3–GeS_2 which is of eutectic type extends, according to Ref. [7], in the range of 0–47 mol% Ga_2S_3. Glassy alloys were synthesized in quartz ampoules from mixtures of binary sulfides of 0.5 g total weight by the direct single-temperature method at 1370 K, kept at this temperature for an hour and into cold water. The glasses of this system are yellow and transparent in the visible spectrum. The alloys with the composition close to eutectic point exhibit the largest affinity for glass formation [8]. Two areas of glass existence were found in Ref. [9] in the Ga–Ge–S system that is separated by the GeS_2–GaS section. They were quenched from 1020 K in the sulfur-rich area, and from 1270 K for the area with high germanium content.

According to Ref. [14], the region of the existence of glasses for quenching from 1170 K is in the middle of the GeS_2–GeS–GaS_{1+k} polyhedron where k = 0 or 0.5. Glasses in the Ga–Ge–S system crystallize easily as evidenced by DTA. Glass formation exists in the range of 0–28 mol% Ga_2S_3 for quenching 2 g batches from 1270 K [13].

The Tl_2S–GeS_2 system features the formation of compounds Tl_4GeS_4, Tl_2GeS_3 and $Tl_2Ge_2S_5$ which melt congruently at 677, 763 and 868 K, respectively [15, 16]. According to Ref. [8], the latter two compounds may be in either crystalline or glassy state. The study of the glass-formation region in the Tl–Ge–S system by quenching the melts in air reported the introduction of more than 30 at.% Tl into the composition of glassy alloys. Macro- and micro-immiscibility regions were found among sulfur-rich alloys. Homogeneous glasses of the compositions around $Tl_xGeS_{1.5}$ were obtained. Their thermal stability decreases substantially with increasing Tl content. The value of the glass transition temperature T_g decreases from 593 to 463 K. The conductivity of glasses increases with thallium content. DTA results on the glasses of the Tl_2S–GeS_2 system presented in Ref. [17] show that adding thallium significantly reduces the glass transition temperature from 786 K for pure GeS_2 to 538 K for the composition $(GeS_2)_{90}Tl_{10}$.

2 Experimental

A total of 55 alloys were synthesized for the investigation of the glass-formation region in the Tl_2S–Ga_2S_3–GeS_2 system. The batches were composed of high-purity elements (at least 99.99 wt%). The samples were placed in quartz ampoules, evacuated to 1.3×10^{-2} Pa, soldered and pre-synthesized by local heating of the ampoules in oxygen-gas burner flame for binding of elemental sulfur under visual observation of the reaction. To prevent splattering during quenching and to reduce losses to the vapor phase condensation, upper parts of ampoule walls were thermostated using the asbestos cord. The ampoules were heated at a rate of 20–30 K/h to 1300 K, held at the maximum temperature for 6 h, and then quenched in cold water.

Glassy state of the alloys was monitored by X-ray phase analysis (DRON 4-13 diffractometer, CuKα radiation) and metallography (Leica VMHT Auto microhardness tester, maximum magnification ×3811).

The characteristic temperatures were determined by differential thermal analysis (Paulik–Paulik–Erdey derivatograph, Pt/Pt-Rh thermocouple, heating at a rate of 10 K/min, cooling in inertial mode).

Optical measurements were performed using an MDR-208 monochromator. Parallel-plane samples of ~0.1 mm thickness with polished surfaces of optical quality were prepared.

3 Results and discussion

Glass-formation region in the Tl_2S–Ga_2S_3–GeS_2 system was determined from the results of the investigation of 55 alloys. All obtained glasses are transparent in the visible region. The color varies from yellow near GeS_2 to rich orange. Most of the prepared samples are located on four rays as shown in Fig. 1.

Under the selected quenching conditions, the glassy alloys at the boundary sides contain up to 66.7 mol% Tl_2S (Ray I in this experiment) and up to 28 mol% Ga_2S_3 according to Ref. [13]. Glass formation stretches to 40 mol% GeS_2 along Ray II, to 30 mol% GeS_2 along Ray III, and to 60 mol% GeS_2 along Ray IV. Diffraction patterns of the glasses of the system along the studied rays are shown in Fig. 2.

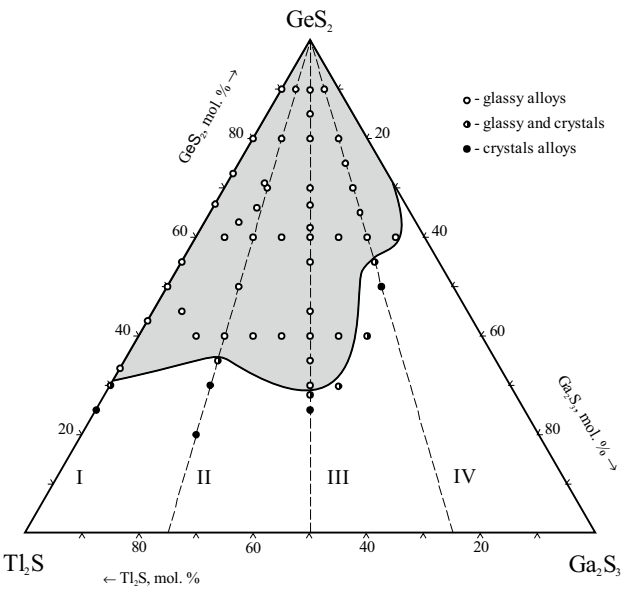

Fig. 1 Glass-formation region in the quasi-ternary system Tl_2S–Ga_2S_3–GeS_2

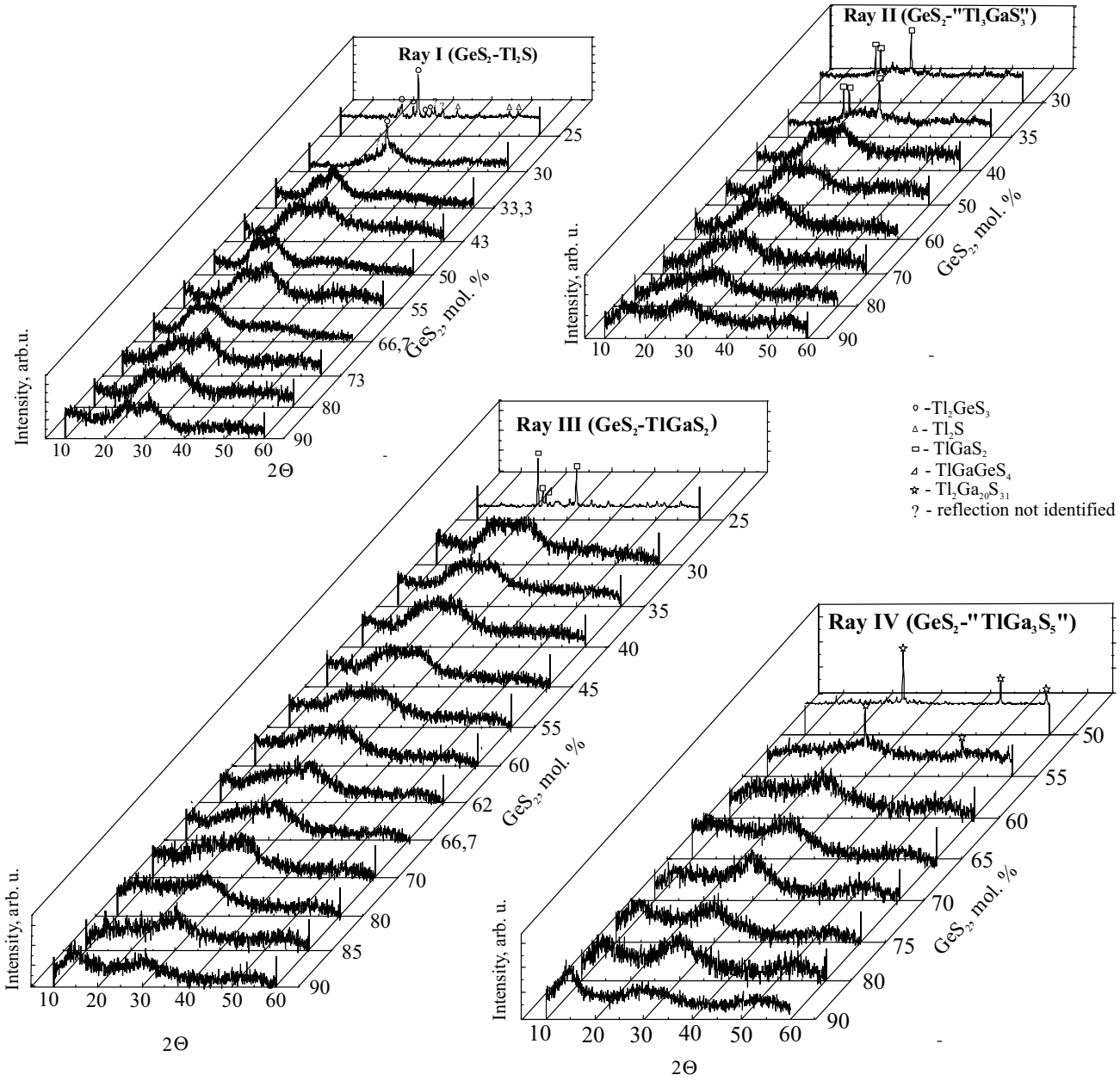

Fig. 2 Diffraction patterns of the glasses of the Tl_2S–Ga_2S_3–GeS_2 system along the investigated rays: *I* GeS_2–Tl_2S, *II* GeS_2–"Tl_3GaS_3", *III* GeS_2–$TlGaS_2$, *IV* GeS_2–"$TlGa_3S_5$" (compositions given in the coordinates of the quasi-ternary system)

Characteristic temperatures were determined for the glassy alloys (glass transition temperature (T_g), crystallization (T_c) and melting point (T_m)), and reduced glass transition temperature was calculated ($T_{gr} = T_g/T_m$) [18]. Here, reduced glass formation temperature is a criterion of the quantitative estimate of the thermal stability of glasses, and relates glass formation temperature T_g and the melting point T_m of the glassy alloys ($T_{gr} = T_g/T_m$). This ratio is determined by the empirical Kauzmann rule or the rule of "two thirds" according to which $T_g/T_m \approx 2/3$ [18]. These data are listed in Table 1.

Room-temperature spectral dependences of the absorption coefficient α on the photon energy 'hν' of the glassy alloys of the Tl_2S–Ga_2S_3–GeS_2 system for the constant GeS_2 concentrations of 90–70 mol% are shown in Figs. 3, 4, and 5.

The introduction of the modifiers Tl_2S and Ga_2S_3 into the glass-forming matrix GeS_2 ($2 \le x \le 33$) is accompanied by the glassy samples by the shift of the absorption edge to the high-energy region of the spectrum. No impurity peaks were detected in the transparency window (in the low-energy region).

Table 1 Characteristic parameters and bandgap energy of the glassy alloys of the quasi-ternary system Tl_2S–Ga_2S_3–GeS_2

No	Alloy composition (mol%)			T_g (K)	T_c (K)	T_m (K)	T_{gr} (K)	E_g (eV)
	Tl_2S	Ga_2S_3	GeS_2					
1	7.5	2.5	90	487	675	960	0.51	2.17
2	15	5	80	489	641	964	0.51	2.21
3	22.5	7.5	70	503	622	814	0.62	2.25
4	30	10	60	532	625	922	0.58	2.22
5	37.5	12.5	50	501	608	883	0.57	2.15
6	45	15	40	499	562	702	0.71	2.06
7	5	5	90	471	765	1025	0.46	2.28
8	7.5	7.5	85	461	757	1033	0.45	2.29
9	2.5	7.5	90	564	804	930	0.61	2.37
10	5	15	80	594	677, 764	945	0.63	2.37
11	6.5	18.5	75	503	727, 763	991	0.51	2.39
12	7.5	22.5	70	569	732, 753	987	0.58	2.26
13	10	30	60	579	706, 743	945	0.61	–
14	22	7	71	523	634	912	0.57	–
15	36	8	66	542	622	921	0.59	–
16	31	6	63	559	639	937	0.59	–
17	35	5	60	491	626	926	0.53	–
18	50	5	45	443	513	709	0.62	–
19	50	10	40	447	540	740	0.60	–
20	27	–	73	502	621	821	0.61	–
21	45	–	55	525	664	723	0.73	–

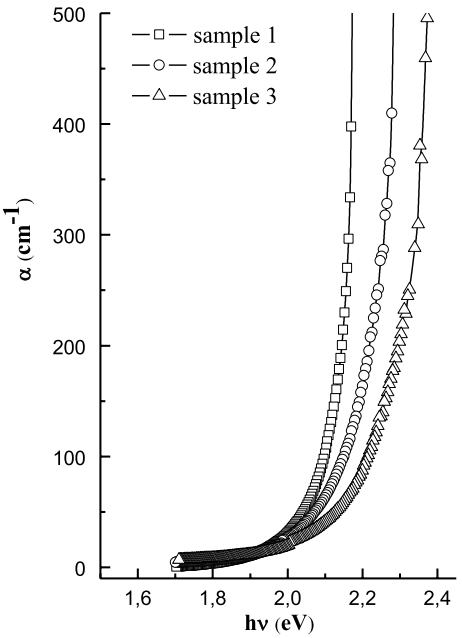

Fig. 3 Spectral dependence of the absorption coefficient: *sample 1* $7.5Tl_2S$–$90GeS_2$–$2.5Ga_2S_3$; *sample 2* $5Tl_2S$–$90GeS_2$–$5Ga_2S_3$; *sample 3* $2.5Tl_2S$–$90GeS_2$–$7.5Ga_2S_3$

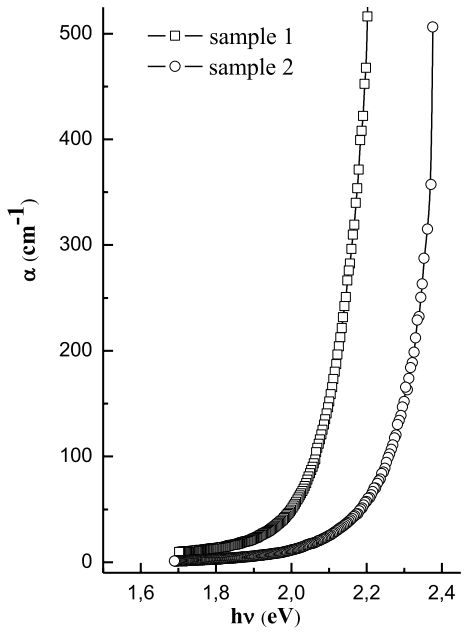

Fig. 4 Spectral dependence of the absorption coefficient: *sample 1* $15Tl_2S$–$80GeS_2$–$5Ga_2S_3$; *sample 2* $5Tl_2S$–$80GeS_2$–$15Ga_2S_3$

Bandgap width E_g was estimated from the spectral distribution of the absorption coefficient at the fundamental absorption edge (for $\alpha \approx 550\ cm^{-1}$). The dependence of E_g on the composition of glassy alloys is given in Table 1.

The increase of E_g with the concentration of Tl_2S and Ga_2S_3 (modifiers) is related, in our opinion, to the distortion of the glass-forming matrix due to the introduction of Tl^+ and Ga^{3+} ions, which have larger radii compared to germanium [19].

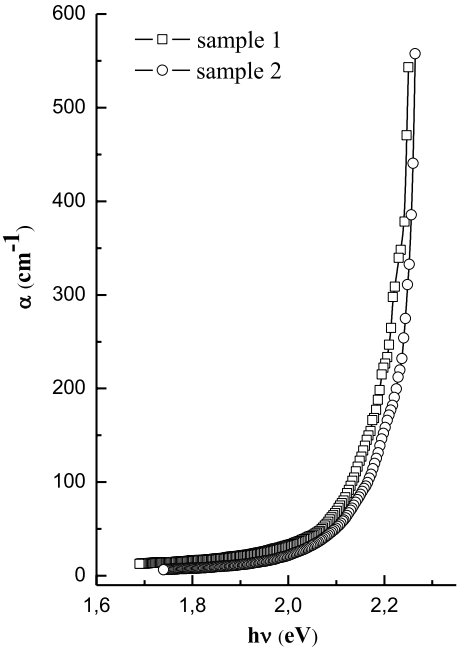

Fig. 5 Spectral dependence of the absorption coefficient: *sample 1* $22.5Tl_2S$–$70GeS_2$–$7.5Ga_2S_3$; *sample 2* $7.5Tl_2S$–$70GeS_2$–$22.5Ga_2S_3$

The site disorder of atomic positions in non-crystalline materials results in the formation of tails of the density of states at the edge of the permitted energy bands which leads to exponential dependence of the absorption coefficient. This exponential dependence of $\alpha(h\nu)$ is observed from the high-energy part of the spectrum indicating the adherence to Urbach's rule that describes the edge of the fundamental absorption band in disordered systems [20–24].

Characteristic energy $\Delta = d(h\nu)/d(\ln\alpha)$ which defines a degree of the absorption edge tailing was determined from the energy dependence of the absorption coefficient and Urbach's rule. The parameter Δ lies for all samples in the range of 0.10–0.20 eV which is consistent with the data of [25, 26] which state that the slope of Urbach's edge $\Delta = 0.05$–0.25 eV for a variety of vitreous systems.

In our case, the value of Δ depends on the composition of glassy alloys. Increasing concentration of Tl_2S and Ga_2S_3 (modifiers) results in an increase of the steepness of the absorption edge (lower tailing) which can be interpreted as a decrease in value of the random potential relief for electrons in the tails of the density of states adjacent to the band edges.

3.1 Photoinduced third harmonic generation

It is well known that for the chalcogenide crystal the nonlinear optical effects of the second and third order may be caused by using even one beam [21], and contrary to the oxide glasses [22] these materials possess a high degree of phonon anharmonicity. The later are descried by the third rank polar tensors and may give a huge contribution to the output nonlinear optical effects, like photoinduced second harmonic generation or third harmonic generation in different materials [25, 27–27].

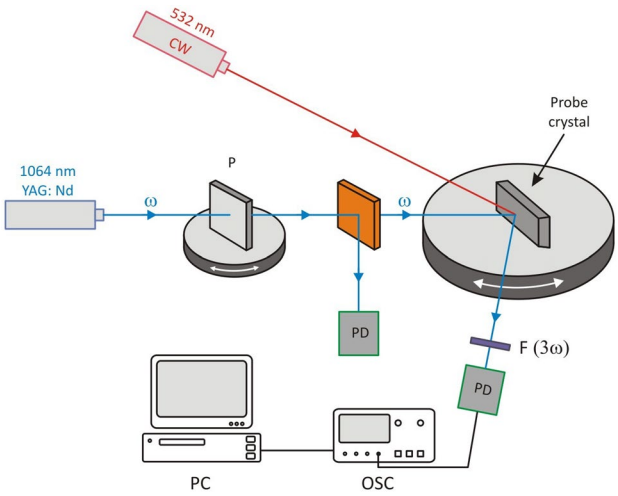

Fig. 6 Principal set-up for the photoinduced THG measurements

Contrary to the other works here we use the photoinducing beam propagating through the bulk part of materials and the detection is performed for the near-the-surface states. The thickness of this layer normally does not exceed 100 nm.

In the Fig. 6 is presented the principal set-up showing the formation of the third harmonic generation (THG). The fundamental beam of nanosecond 1064 pulsed laser with varied power density was incident o the sample.

In the present work, we have used the photoinducing 532 nm laser beams with power 200 mW, beam diameter about 3 mm penetrating within the forbidden gap. The control of the photoinduced changes was performed using the probing fundamental beam penetration of the samples at 1064 nm and the output nonlinear optical beam is located mainly near the surface states at 355 nm. As a consequence, the principal role here is played by the gradient of absorption the near-the-surface states due to the high absorption for the output third harmonic generation at 355 nm wavelength.

The 355 nm interferometric filter has spectrally cut the output THG with respect to the incident light. The fast response photomultiplier has registered the quick temporary changes of the output THG signal using an oscilloscope with 1 GHz resolution.

In the Fig. 7 are presented the typical THG in the reflected regime before and after the illumination. The beam sequence of the photoinducing beam has completely overlapped with the probing Nd:YAG laser beam. The thermo-heating did not exceed 3 degrees.

One can see that the enhancement achieves up to 30%. After switching off of the photoinducing laser the effect was

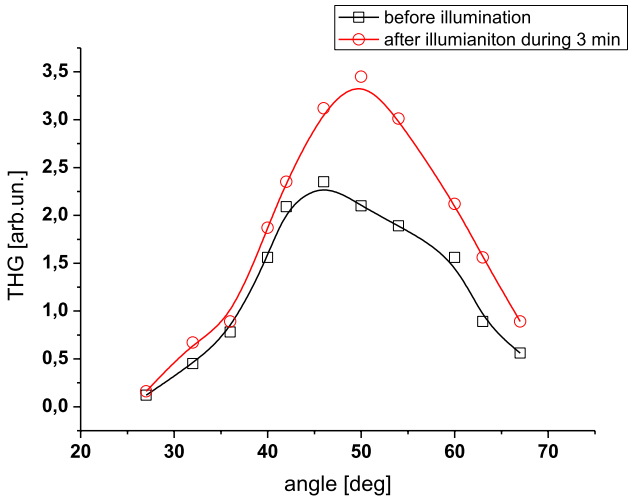

Fig. 7 Typical dependence of THG versus incident angle

decayed during the several milliseconds. The content of the glasses did not play any role.

4 Conclusions

In summary, we have discovered a huge enhancement of the third harmonic generation during illumination by the green CW laser operating at 532 nm for the studied chalcogenide glasses. The tripled frequency signal of fundamental nanosecond beam at 1064 nm was enhanced up to 30% during a few minutes illumination by 200 mW green CW laser. The decrease of the effect is about several milliseconds which may be used for optical triggered optoelectronic systems. It is crucial that the changes on the content did not change the principal features.

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