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Glass formation and the third harmonic generation of Cu_2Se–$GeSe_2$–As_2Se_3 glasses

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We have performed the investigation of the nonlinear optical properties namely the third harmonic generation (THG) of the glass-formation region in the Cu_2Se–$GeSe_2$–As_2Se_3 system. The samples were synthesized by direct single-temperature method from high-purity elementary substances. We have found that the value of disorder parameter Δ depends on the composition of the glassy alloys. The measurements show that increasing the Cu_2Se concentration leads to increased slope of the absorption edge, which may be explained by the decrease of the height of random potential relief for the electrons in the tails of the state density which border the band edges. A very sharp increase in the THG at low temperature was observed. Significant enhancement in THG was obtained with decreasing the energy gap, which agreed well with the nonlinear optical susceptibilities obtained from other glasses. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4897457]

I. INTRODUCTION

Germanium (IV) selenide, along with arsenic (III) selenide, is used as the model objects for the investigation of the role of near and far order in the formation of the electron and vibrational spectra and the electron properties of semiconductors. The interest to germanium-based glassy semiconductors of more complex composition (binary and ternary) is caused by the promising application for optical and holographic memory.[1] These compounds ($GeSe_2$ and As_2Se_3) are also good glass-forming elements.[2–4] Their interaction results in a continuous glass-formation region.[5] The introduction of copper into the chalcogenide glassy materials based on the $GeSe_2$–As_2Se_3 alloys is reported to change substantially their properties due to the change of the structure of glasses.[6–8]

The investigation of the optical absorption spectra for a large glass-formation region is a powerful tool to study the electronic structure of the glassy semiconductors and of the forecasting of their physical properties.

II. EXPERIMENTAL

The investigation of the glass-formation region in the Cu_2Se–$GeSe_2$–As_2Se_3 system was performed on 73 samples that were synthesized by direct single-temperature method from high-purity elementary substances. The maximum synthesis temperature was 1373 K. The samples were quenched into room-temperature water. The alloys were investigated by X-ray phase analysis (DRON 4–13 powder diffractometer, CuK_α radiation, $10° \leq 2\theta \leq 90°$, step scan mode with a step size of 0.05° and counting time of 1 s per data point), differential-thermal analysis (Paulik–Paulik–Erdey system derivatograph, Pt/Pt-Rh thermocouple), and metallography (MMU-3 microscope and Leica VMHT Auto microhardness tester). Optical measurements were performed using an MDR-208 monochromator on parallel-plane plates of ~0.1 mm thickness with optical quality polished surface. The absorption spectra were investigated in the $h\nu$ range of 1.0–2.0 eV. The third harmonic generation (THG) measurements were performed at 1540 nm wavelength.

III. RESULTS

The glass-formation region of the quasi-ternary system Cu_2Se–$GeSe_2$–As_2Se_3 is shown in Fig. 1. The glassy state was determined by (1) the absence of the reflections on the diffraction patterns and the presence of halos; (2) the uniformity of the polished surface under the metal microscope observation; (3) the characteristic shape of the differential curves of heating and cooling. The glass-formation region stretches along the quasi-binary system $GeSe_2$–As_2Se_3 widening to 35 mol. % Cu_2Se with the increase of the As_2Se_3 content (Fig. 1). Lines of isotherms join the samples with the close values of the glass formation temperature.

Table I presents the compositions of the samples in the order of decrease the As_2Se_3 content, the results of differential thermal analysis and microhardness measurements. Their

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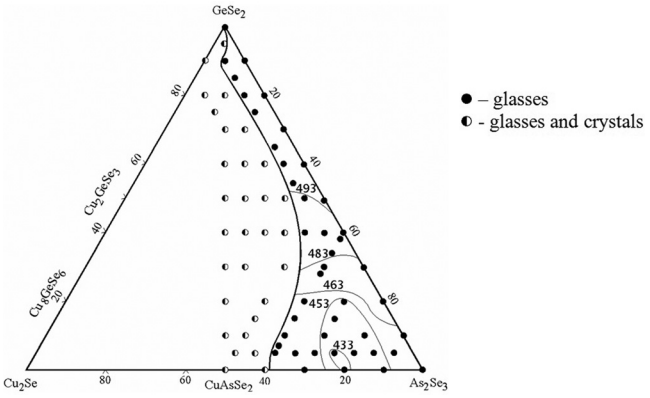

FIG. 1. The glass-formation region of Cu_2Se–$GeSe_2$–As_2Se_3 system.

physico-chemical characteristics (glass formation temperature T_g, crystallization temperature T_c, melting point T_m, microhardness H) increase with the $GeSe_2$ content. The calculated reduced glass formation temperature ($T_{gr} = T_g/T_m$), which characterizes the affinity of the alloys to glass formation, is also presented in Table I (according to Kausmann criterion, $T_{gr} \approx 2/3$ (Ref. 9)).

A. The optical properties

Six glassy samples with the 60 mol. % As_2Se_3 concentration were selected for the investigation of the optical properties (Table II). The absorption spectra were investigated in the $h\nu$ range of 1.0–2.0 eV.

The dependences of the absorption coefficient α on the phonon energy hν at room temperature are presented in Fig. 2.

The introduction of the modifier Cu_2Se ($2 \leq x \leq 33$) into the glass-forming matrix $GeSe_2$–As_2Se_3 results in the shift of the absorption edge to the lower-energy part of the spectrum. No admixture maxima were found in the transparency region.

The bandgap energy E_g was estimated from the spectral distribution of the absorption coefficient in the absorption edge region (as the energy of the quanta for which $\alpha = 450\,cm^{-1}$). The dependence of E_g on the composition of the glassy alloys is given in Table II.

The decrease of E_g with the increase of the Cu_2Se concentration is related, in our opinion, with the deformation of the glass-forming matrix upon the introduction of Cu^+ ions which have larger radius compared to germanium and arsenic.[10]

A consequence of the site disorder of non-crystalline materials is the formation of the tails of state density at the edges of the permitted energy bands which is exhibited in the exponential dependence of the absorption coefficient. Such exponential dependence of $\alpha(h\nu)$ may be found at the high-energy side of the spectrum which follows Urbach's law that describes the fundamental absorption edge of the disordered systems.[11]

Using the energy dependence of the absorption coefficient and Urbach's law, we determined the characteristic energy ($\Delta = d(h\nu)/d(\ln\alpha)$) which shows the degree of tailing of the absorption edge. The parameter Δ of all investigated samples lies in the range of 0.10–0.16 eV (the parameters of the slope of Urbach's edge for various glassy systems range from 0.05 to 0.25 eV).[11,12]

TABLE I. The composition and the properties of glasses of the Cu_2Se–$GeSe_2$–As_2Se_3 system.

	Composition, mol. %							
№	Cu_2Se	$GeSe_2$	As_2Se_3	Tg, K	Tc, K	Tm, K	H, GPa	Tgr
1	…	…	100	458	612	…	…	…
2	10	…	90	451	584	626	146	0.72
3	5	5	90	457	594	…	119	…
4	…	10	90	464	…	…	131	…
5	10	5	85	442	574	…	…	…
6	20	…	80	421	540	668	115	0.63
7	15	5	80	443	568	…	145	…
8	10	10	80	449	598	…	146	…
9	…	20	80	471	723	…	120	…
10	20	5	75	431	599	…	145	…
11	30	…	70	459	501	684	…	0.67
12	25	5	70	457	566	674	…	0.67
13	20	10	70	453	513	761	141	0.60
14	15	15	70	448	524	782	…	0.57
15	10	20	70	449	594	786	104	0.57
16	…	30	70	480	…	717	…	0.67
17	30	5	65	454	524	693	…	0.66
18	35	5	60	464	603	686	…	0.67
19	30	10	60	459	620	692	…	0.66
20	25	15	60	460	…	673	…	0.68
21	20	20	60	465	645	692	…	0.67
22	10	30	60	483	697	827	138	0.58
23	…	40	60	491	…	739	…	0.66
24	5	40	55	484	607	803	137	0.60
25	10	40	50	459	617	847	146	0.54
26	…	50	50	504	…	758	136	0.66
27	5	50	45	494	679	823	143	0.60
28	5	55	40	498	733	843	…	0.60
29	…	60	40	530	…	788	141	0.67
30	5	60	35	504	726	844	173	0.60
31	5	65	30	517	686	863	…	0.60
32	…	70	30	560	…	798	142	0.70
34	5	75	20	527	678	852	177	0.62
35	…	80	20	580	…	825	149	0.70
36	5	80	15	600	680	892	184	0.67
37	5	85	10	616	676	905	205	0.68
38	…	90	10	604	822	910	217	0.66
39	5	90	5	560	790	…	…	0.71
40	…	100	…	655	833	1010	162	0.65

TABLE II. Bandgap energy of the glassy alloys of the Cu_2Se–$GeSe_2$–As_2Se_3 system at 292 K (determined at $\alpha = 450\,cm^{-1}$).

	Composition, mol. %			E_g, eV
№	Cu_2Se	$GeSe_2$	As_2Se_3	
1	33	7	60	1.22
2	30	10	60	1.28
3	25	15	60	1.33
4	12	28	60	1.41
5	6	34	60	1.53
6	2	38	60	1.64

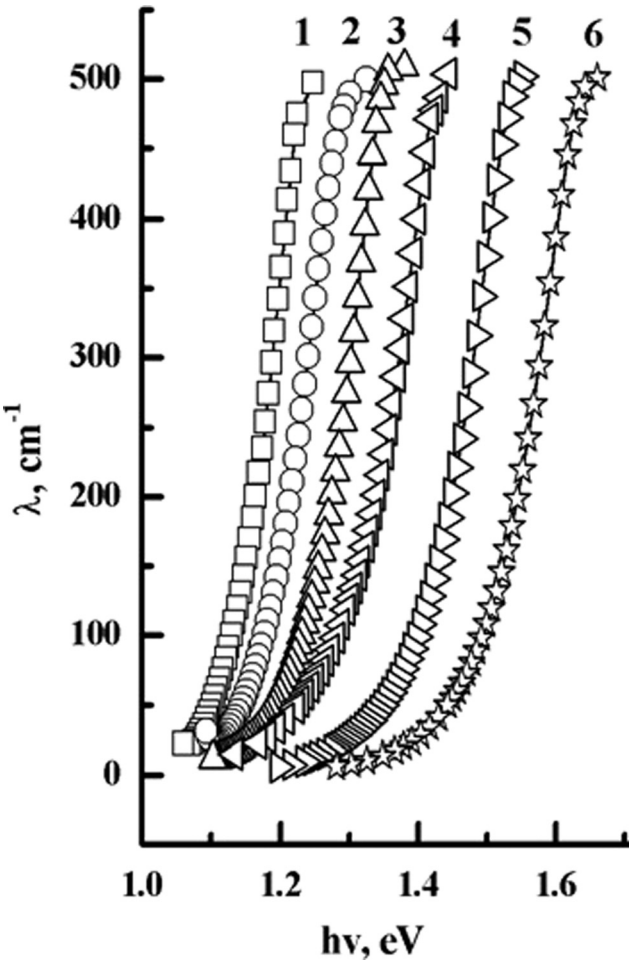

FIG. 2. Dependence of the absorption coefficient on the phonon energy at 292 K: (1) 33 mol. %Cu_2Se–7 mol. %$GeSe_2$–60 mol. %As_2Se_3; (2) 30 mol. %Cu_2Se–10 mol. %$GeSe_2$–60 mol. %As_2Se_3; (3) 25 mol. %Cu_2Se–15 mol. %$GeSe_2$–60 mol. %As_2Se_3; (4) 12 mol. %Cu_2Se–28 mol. %$GeSe_2$–60 mol. %As_2Se_3; (5) 6 mol. %Cu_2Se – 34 mol. %$GeSe_2$–60 mol. %.

The value of Δ depends on the composition of the glassy alloys. The less disordered from this viewpoint are the glassy alloys that contain 33 mol. %Cu_2Se–7 mol. %$GeSe_2$ – 60 mol. %As_2Se_3. The increase of the Cu_2Se concentration leads to increased slope of the absorption edge, which may be explained by the decrease of the height of random potential relief for the electrons in the tails of the state density which border the band edges.

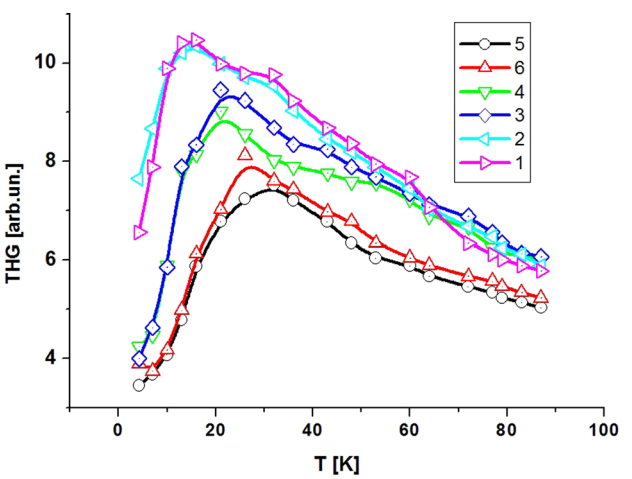

FIG. 3. Dependence of the third harmonic generation for the fundamental wavelength 4.6 mm for the studied Cu_2Se-$GeSe_2$-AS_2Se_3 glasses versus the temperature.

The dependence of THG on temperature was investigated for these samples for the fundamental wavelength of 4.6 μm. Following Fig. 3, one can see an asymmetry in temperature dependence of THG. At the lower temperatures, there is observed very sharp increase of the THG. One can see that with decreasing of energy gap, there is an enhancement in the THG which is in agreement with the nonlinear optical susceptibilities obtained for other glasses.[13–17] It was established that decreasing of energy gap leads to increasing THG efficiency which is typical for third order nonlinear optical susceptibilities.

IV. CONCLUSIONS

The nonlinear optical investigation of the glass-formation region in the Cu_2Se–$GeSe_2$–As_2Se_3 system was performed. The samples were synthesized by direct single-temperature method from high-purity elementary substances. The value of disorder parameter Δ depends on the composition of the glassy alloys. The less disordered from this viewpoint are the glassy alloys that contain 33 mol. %Cu_2Se–7 mol. %$GeSe_2$–60 mol. %As_2Se_3. The increase of the Cu_2Se concentration leads to increased slope of the absorption edge, which may be explained by the decrease of the height of random potential relief for the electrons in the tails of the state density which border the band edges. At the lower temperatures, there is observed very sharp increase of the THG.

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