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Photoinduced nonlinear optical phenomena in Sb_2Se_3-$BaCl_2$-$SnCl_2$ glasses

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Photoinduced nonlinear optical phenomena have been studied in amorphous Sb_2Te_3-$CaCl_2$-$SnCl_2$ glasses using photoinduced optical second harmonic generation (SHG). The photoinduced SHG signal was measured for double frequency of a CO_2 laser ($\lambda = 5.3$ μm) using a photoinducing CO laser ($\lambda = 5.5$ μm). We have found that the SHG signal intensity increases with increase of the CO laser photoinducing exposure and achieves its maximum value after 1.5 h. Absolute values of the SHG signals were more than one order in magnitude smaller comparing to a χ_{222} tensor component for the ZnSe single crystals. The SHG signal strongly increases if temperature decreases from 39 to 16 K. Femtosecond probe-pump measurements indicate existence of the SHG maximum at pump-probe time delay of about 43 ps. It is suggested that Sb-Se tetrahedra play a key role in the observed photoinduced nonlinear optical effects. Degree of noncentrosymmetry of corresponding bonds depends on time of the CO-laser illumination, temperature and mechanical stresses. Simultaneously, the investigated glasses can serve as promising materials for a femtosecond IR quantum electronics.

1. Introduction

Oxygen-free glasses were subject of increasing interest in last few years [1–3] because of their possible use in different branches of IR optoelectronics, holography and IR quantum electronics materials engineering. Light transmission coefficients between 36% and 57% have been observed for wavelengths from 0.65 to 49 μm. A main purpose of present paper consists in investigations of the new synthesized glasses as materials for nonlinear optical devices in IR spectral region. An original IR photoinduced setup (see Fig. 1) have been proposed for the mentioned measurements. More details of the measurement setup as well the specimen preparation is presented in the Section 2. In the Section 3 are given experimental results for the photoinduced SHG versus the CO-laser photoinducing exposure, delaying time between the photoinducing and probing beams, pressure and temperature.

2. Experimental details

A glass formation region of the Sb_2Se_3-$BaCl_2$-$SnCl_2$ system is shown in Fig. 2. The above mentioned region is situated near a point of binary Sb_2Se_3-$SnCl_2$ system. An upper and lower limit of Sb_2Se_3 concentration for the bulk glass formation is 75 and 46 mol %, respectively. A third compound of $BaCl_2$ enhances this glass formation tendency of the binary system. The binary system of Sb_2Se_3-$BaCl_2$ cannot form itself a bulk glass because of larger field strengths of Ba^{2+} ions.

The Sb_2Se_3-$SnCl_2$-$BaCl_2$ glass was prepared using 5 parts of NbSb powder, 5 parts of NSe beads and anhydrous halides of $BaCl_2$ and $SnCl_2$. The raw materials were weighed, mixed and placed into a silica glass tube with a sealed end. The silica glass tube was then evacuated to a vacuum of about 10^{-2}–10^{-3} Pa and sealed. The tube was heated at about 650–670 °C for 5 h in an electric furnace. During melting the silica glass tube was shaken to mix a glass melt. The glass melt was quenched in water at temperature of 20–25 °C together with the silica glass tube. The glass formation and the structural investigations of the obtained glasses were conducted by the X-ray diffraction method, including a phase analysis, an analysis of the radial distribution function (RDF) and infrared absorption spectroscopy (IR method).

DTA measurements have given the following parameters a verification temperature $T_g = 238$ °C; crystallization temperatures $T_{c1} = 304$ °C and $T_{c2} = 388$ °C; a melting temperature of a crystalline phase $T_m = 398$ °C.

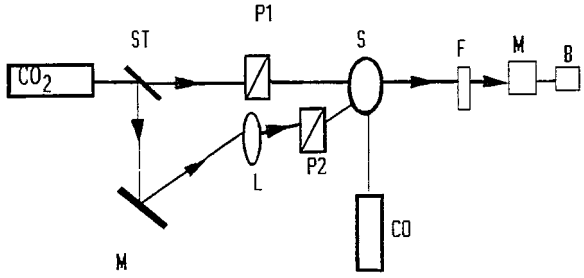

Figure 1 An apparatus for experimental investigations of photoinduced SHG.

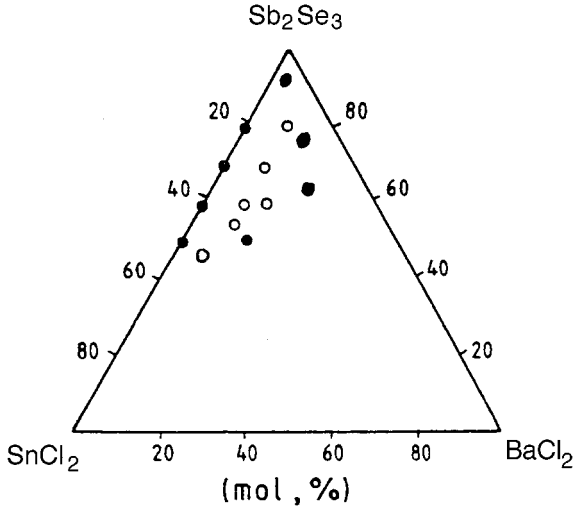

Figure 2 A glass formation region of the Sb_2Se_3-$SnCl_2$-$BaCl_2$ system.

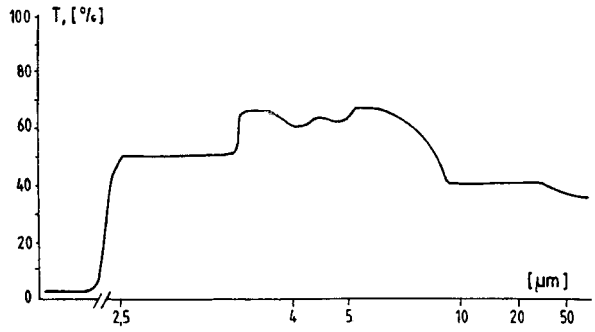

Figure 3 IR transparency spectra of the investigated glasses.

The IR spectra show a wide transparency band (Fig. 3). A typical radial distribution function (RDF) of a sample glass shows two main peaks located at 0.282 nm and 0.403 nm. The position of the former peak can be attributed to bond lengths of Sb-Se and Sb-Cl atomic pairs, while the position of the latter peak can be attributed to interatomic distances within Sb-Sb, Se-Se, Sn-Sn, Ba-Ba, Sn-Cl and Cl-Cl pairs. Unfortunately, it is difficult to determine the atomic distances of each pair and coordination numbers of the cations because of such complicated composition of the investigated glass.

The glass formation region of Sb_2Se_3-$SnCl_2$-$BaCl_2$ system has been obtained showing a better glass formation ability than other Sb_2Se_3-based glasses with halogen univalent cations. Light transmittance for wavelengths between 0.65 and 50 μm and other technological properties of these glasses support a statement that they represent suitable materials for infrared optic fibers. The halide-chalcogenide glasses on the basis of Sb_2Se_3 are important from application point of view.

Since structural rearrangements induce changes in localized-state distributions of the material, the measurements of the transient SHG signals are of considerable importance to understand the photoinduced metastable states in amorphous glasses.

Results of the optical transient second harmonic generation (SHG) study have been obtained for IR-light induced non-centrosymmetry structural fragments in the amorphous Sb_2Se_3-$SnCl_2$-$BaCl_2$ glasses. We have also compared metastable states for systems of different contents and analyzed their high-resolved time dependencies.

Experimental investigations of the photoinduced SHG have been performed. A typical sample has a form of plate with thickness of 5 mm and surface area of about 1.7 cm^2. As a source of the photoinduced changes a CO-laser ($\lambda = 5.5$ μm) was used with a photon flux of 10^{18}–10^{19} photon/cm^2. An upper power restriction is necessary to avoid sample overheating. Intensity at a specimen position was checked using a commercial fast-response joulemeter (Genetic, Inc, model ED-200).

Using a ZnSe splitter and proustite delaying cell, the light beam is splitted in two beams of wavelength of 10.6 μm. Our apparatus (Fig. 1) allows us to change the delay time between the pump and probe beam. It is also possible to modify intensity of the light flux. The measurements have been carried out for polarized light obtained by use of a KBr-NaCl polarizer. A maximal intensity of the output SHG signal was achieved for parallel directions of the probe and the input CO_2-laser beams.

A separation between the output SHG ($\lambda = 5.3$ μm), photoinducing CO-laser ($\lambda = 5.5$ μm) and pump beam was achieved using an IR grating monochromator of IRG-8.96-M type. The SHG intensity was detected using a RIR-34 IR bolometer. The measurements were carried out in a single-pulse regime (with a pulse repetition frequency of 7 Hz). A pyrargiryt single-crystal cell (cut in a plane of optic axis) was applied as an intensity standard. The time-dependent SHG signals were measured using a high-time-resolved spectroanalyzer SA-165.

3. Results and discussion

We have measured dependences of the photoinduced SHG intensities versus the photoinducing CO-laser illumination time (Fig. 4). The SHG intensity increases with increase of the CO-laser illumination time and achieves its maximum after approximately 1.5 h for the flux of 14×10^{13} photon/cm^2. In our opinion, such a behaviour reflects occurrence of noncentrosymmetry metastable structural components due to the CO-laser induced photo-generation. The observed phenomena are caused by the photo-generation of electrons

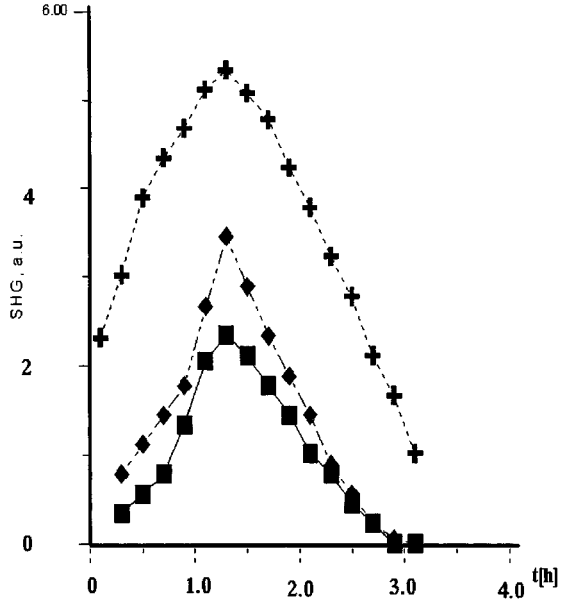

Figure 4 Dependence of PISHG as a function of time of CO-laser photon flux at different photoinducing flux (in photon/cm^2): □, 12×10^{19}; ◇, 12×10^{11}; +, 14×10^{13}.

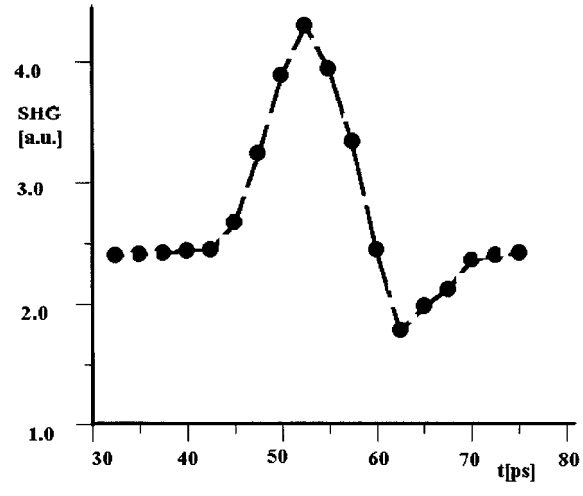

Figure 5 Dependence of output SHG as a function of time delay between the probe and pump beam.

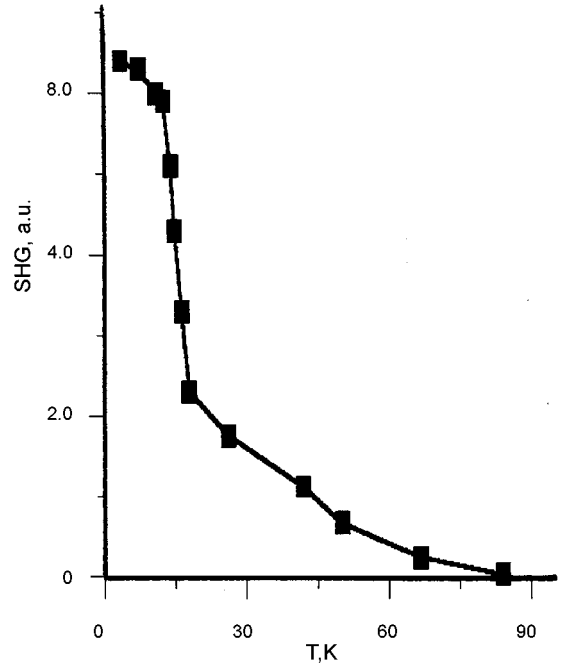

Figure 6 Temperature dependence of the photoinduced SHG at delaying time of about 50 ps.

(and appropriate vibrations, i.e., quasi-phonon modes) from occupied states to unoccupied (conduction) states.

If the photoinducing CO-laser power increases more and more, then the third harmonic generation (THG) becomes more probable. Such phenomena are described theoretically by fourth rank tensors and they dominate for a photon flux of about 11×10^{16} photon/cm^2 that can be caused by destruction of the lower excited states by CO-laser light. A separate paper will be devoted to such investigations. The most typical examples of the dependences for the Sb_2Se_3-$SnCl_2$-$BaCl_2$ specimens are presented in Fig. 4 and other samples show a similar behaviour. It should be pointed out that the obtained dependencies are asymmetric.

Values of the SHG intensity are more than one order in magnitude smaller comparing to the ZnSe single crystals in the case of its χ_{222} tensor components. Time of the photoinduced SHG signal did not exceed 1.5 ps. A maximal signal was achieved for a delay time between the pump and probe beams of about 43 ps (Fig. 5). This reflects an essential role of the electronic subsystem in appearance of the photoinduced SHG.

An important aspect of the investigated phenomena consists in temperature dependencies of the photoinduced SHG (Fig. 6). The investigations of all samples have shown an enhancement of the SHG signal with decreasing temperature below 38 K. According to this behavior, one can suggest occurrence of the low-temperature structural rearrangements of the Sb-Se pyramidal bridges caused by low-temperature thermoactivation processes. The results have unambiguously confirmed essential role of the Sb-Se vibrations in formation of the metastable non-centrosymmetry states because experiments performed for samples without the Sb-Se groups have shown a vanishing effect on the output SHG signal. Therefore, one can expect that these bonds mainly contribute to the observed SHG. The essential role of the electron-quasiphonon interactions in the nonlinear optical effects will be subject of a separate work. Special theoretical as well as experimental investigations are required for this purpose.

Dependencies of the photoinduced SHG intensities are presented in Fig. 7 for the above mentioned glass samples as functions of duration time of a mechanical stress. It is clearly seen that a maximal value of the SHG intensity is obtained for glasses treated by the external mechanical stresses of 5 N/cm^2 during 20 min (and applied in parallel to a surface plane). The upper limit is avoided by a mechanical reliability of the specimen. The PISHG signal saturates after 14 min and then slowly decreases.

A correlation between the time of mechanical treatment and the output SHG signal has been unambiguously found. A saturation of the SHG signal was achieved after 10 min of such treatment. One can expect

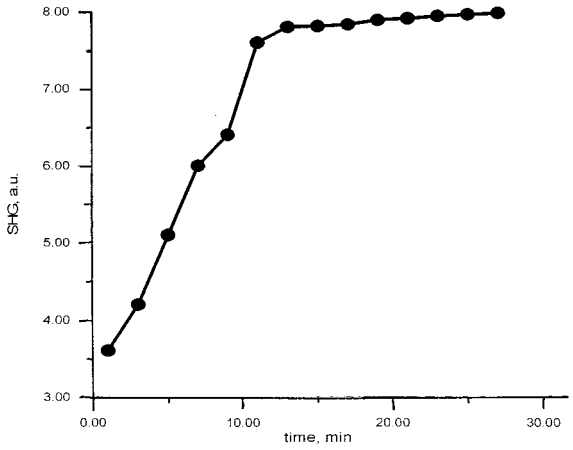

Figure 7 Dependence of the photoinduced SHG on time after a mechanical treatment for pressure of 5 N/cm^2.

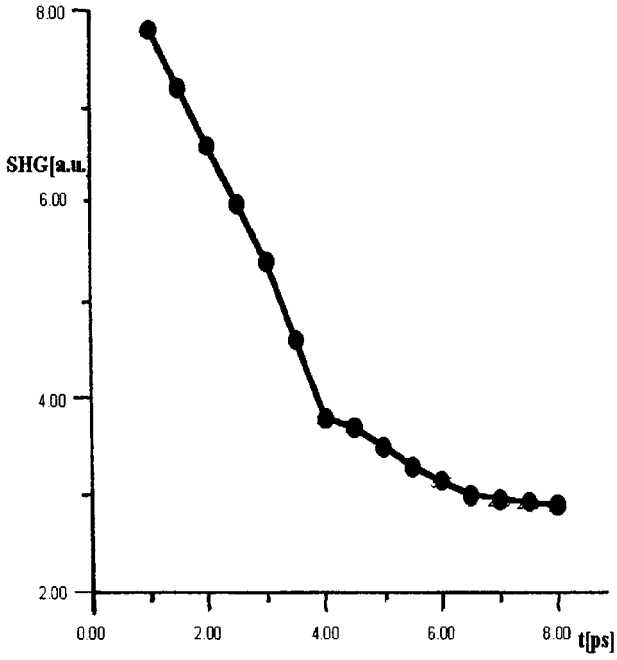

Figure 8 Time-resolved dependence of the photoinduced SHG signal averaged within a low-temperature range.

that the increasing mechanical treatment stimulates appearance of additional non-centrosymmetry due to different elastic constants of particular chemical bonds in the glass system. In the result, we have observed the SHG intensity that is caused by the mechanically induced local structural noncetrosymmetry.

The appearance of the PISHG saturation is mainly connected with a saturation of corresponding photo-orientational processes. The similar behavior has been observed under influence of the mechanical uniaxial stresses. This indicates important role of the chemical bonds which are sensitive to influence of these mechanical fields.

Time-resolved dependencies of the SHG maxima attenuation are presented in Fig. 8 for these samples. We have observed no slopes within a time region between 4.1 and 6.5 ps that indicates presence of, at least, three different physical mechanisms, contributing to the output PISHG. It is expected that an essential role belongs to the electron decay of exciting states below 4.1 ps, while the quasi-phonons interacting with the electronic subsystem take part for times above 4.1 ps.

Our investigations have unambiguously shown the appearance of the photoinduced SHG signals described by the third-rank polar tensors. Several mechanisms can serve to explain this phenomenon. The first one consists in photo-orientational (or piezo-orientational) deformations resulting from photo-chemical (piezo-induced) reactions that leads to appearance of the non- centrosymmetric structural components (and corresponding polar tensors). The second possibility may be an electric quadrupolar interaction which is allowed in the centrosymmetric systems but it is usually weak. These two mechanisms are able to produce (in a coherent way) a light beam of double frequency being collinear with the pump laser beam.

However, an incoherent localized SHG random irradiation (propagating in all directions and caused mainly by a second-order Rayleigh scattering hyperpolarizability) can not be in full excluded. To avoid such influence of the hyper-Raman scattering, we have performed additional investigations of light scatterring for wavelengths from 5500 to 10600 nm. We have detected two hyper-Raman maxima at 3300 and 7600 nm which intensities were, at least, 7 times weaker than the orientational SHG intensity. It was also found that the intensity of this light was two orders in magnitude weaker than the SHG intensity.

4. Conclusions

We have revealed, for the first time, the essential influence of IR CO-laser light on the nonlinear optical susceptibilities in Sb_2Te_3-$CaCl_2$-$SnCl_2$ glasses. We have found that the SHG intensity increases with increase of the CO-laser exposure time and achieves its maximum after 1.5 h for a light flux of 14×10^{13} photon/cm^2 and a pump-probe delay time of about 43 ps. The absolute SHG values were more than one order in magnitude smaller comparing with the ZnS single crystals in the case of its χ_{222} ($\lambda = 10.6\ \mu$m) tensor components. The relaxation time of the photoinduced SHG signal did not exceed 1.5 ps.

Special investigations have shown that one can observe the enhancement of the SHG below 38 K. According to this behaviour, one can say about occurrence of the low-temperature structural rearrangements of the Sb-Se pyramidal bridges caused by low-temperature thermo-activation processes. The essential role of the Sb-Se vibrations can be observed in formation of the metastable non-centrosymmetry states. Therefore, it is expected that these bonds give a main contribution to the observed PISHG. One can also expect an essential role of the electron-phonon contribution to the observed nonlinear optical effects.

We have revealed that the maximum value of the photo-induced SHG signal can be obtained in the case of the investigated glasses if one treats them during 20 min by external mechanical stresses (applied in parallel to a surface plane) of 5 N/cm^2. The upper limit is avoided by the mechanical reliability of the specimen. The PISHG signal saturation should be underlined.

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