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IR Photoinduced Piezoelectric Effects in Multi-Component Chalcogenides $\text{Ag}_2\text{In(Ga)_2Si(Ge)S(Se)}_6$

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The influence of external irradiation of $\text{CO}_2$, CO, Er:glass, Nd:YA lasers on the piezoelectric properties of the $\text{Ag}_2\text{In(Ga)_2Si(Ge)S(Se)}_6$ crystals was investigated. The maximum photoinduced changes in the piezoelectric coefficient were observed after irradiation with $\text{CO}_2$ laser. CO photoinducing bicolour beams with 5.5 $\mu$m wavelength cause at least 4 times smaller increase in piezoelectric coefficients. Therefore, it can be expected that the primary mechanisms cause the excitation of the phonon subsystem.

Keywords: chalcogenides, laser, photoinduced piezoelectric properties.

Introduction

An increased interest in the creation of optically controlled devices for the use as optical triggers in a wide spectral range is recently observed [1, 2]. The search and design of various types of sensors that convert mechanical energy into electricity stimulated intensive study of piezoelectric materials. The attention among such types of materials is attracted to such promising ceramics as $\text{PbZrTiO}_3$, binary semiconductors ($\text{ZnO, GaN, InN}$), both bulk and low-dimensional nanoblocs.

Another direction of research is based on the control of the piezoelectrics by the laser action [3]. This effect was already observed in borate crystals [4] and other chalcogenides [5].

The theoretical evaluations in [6] show that laser-induced electric polarization can be much higher than electro-optical coherent polarization (optical straightening) which consists of generating a direct electric field when passing through a substance.

I. Setting the problem

Due to the specific origin of the chemical bonds, some of the best materials for laser-operated piezoelectrics are chalcogenide crystals [7] and, partially, crystalline glasses [8] which demonstrated the exceptional ability to be controlled by the external light. Chalcogenide crystals have very important anion subsystem which produces additional contributions due to strong phonon anharmonism [9].

One of the main reasons for the use of chalcogenide crystals as laser materials is the large number of intrinsic non-stoichiometric defect states the energy levels of which are located in the band gap. These effectively interact with external laser radiation which resonates with their energy positions thus creating great potential for improving optical polarizations. Therefore, one can expect that the future strategy for the optimization of piezoelectric parameters should be directed to corresponding changes in the cationic subsystem which will enable to achieve a large number of localized disordered electronic states inside the band gap and will determine their effective interaction with the phonon subsystem.

Most studies of laser-induced piezoelectrics were performed in the near-infrared region of the spectrum with wavelengths usually below 3 $\mu$m. Therefore, the main origin of the effect is due to the laser-electron polarization of the electron clouds in the crystals. The phonon subsystem excited by the photo-induced phonons is of secondary value [10, 11]. However, large phonon anharmonisms in chalcogenide crystals [12] lead one to expect that the excitation by mid-IR radiation, e.g., a microsecond $\text{CO}_2$ laser at a wavelength of 10.6 $\mu$m, can
cause direct excitation of phonon anharmonic resonances which are described by the third-rank tensors. It is important to avoid overheating of samples, for instance, by using modulated light. Therefore, we considered the possibility of changing the piezoelectric properties of chalcogenide crystals by the irradiation with both a CO$_2$ pulse microsecond laser that effectively excites the phonon subsystem and lasers whose application will lead to dominating electron photopolarization, namely Nd:YAG (1064 nm), Er:glass (1540 nm).

II. Setting up tasks

Therefore, the work considered the experimental possibility of changing the piezoelectric coefficients by the excitation by pulse CO$_2$, CO, Nd:YAG and Er:glass lasers using two coherent beams at different incidence angles. This may contribute to the emergence of some anisotropic lattices with periods of multiple wavelengths. Experimental results for other chalcogenides showed high stability and efficiency of such lattices [13].

III. Experimental Approach

Piezoelectric studies were performed using piezoelectric $d_{33}$-meter (APC International, Ltd.) which allows the measurement of the piezoelectric module in the range of 1–200 pC/V with an accuracy of 0.1 pC/V and ±2% error. The experimental setup for the piezoelectric studies was the same as described in [14]. The temperature dependence of the piezoelectric coefficient was measured using a thermocouple for the range of 293–357 K with temperature stabilization of 0.02 K. Laser-induced piezoelectric effect was studied using a cw Nd:YAG laser diode and a corresponding light with doubled frequency. The power of this laser varied in the range of 200 – 400 mW. The photon energy of 532 nm lies above the edge of the absorption band of the studied crystals which confirms the predominant electronic origin of photoinduced changes in the observed piezoelectric coefficients since the corresponding resonances are far from the resonances of light.

IV. Results and discussion

We investigated the piezoelectric properties of the Ag$_2$In(Ga)$_2$Si(Ge)Se$_6$ crystals. They were found to be significantly weaker than those of the Ag$_x$Ga$_{1-x}$Se$_2$ compounds. For instance, the $d_{eff}$ value for Ag$_2$In$_2$SiS$_6$ is about 0.9 pm/V, that of Ag$_2$In$_2$SiSe$_6$ is 1.1 pm/V [15]. For comparison, these coefficients are 35.8 pm/V [16, 17] for AgGaGe$_3$Se$_8$. Therefore, the study of piezoelectric properties under the irradiation by two coherent laser beams was performed.

The use of light is a powerful tool for the continuous change of the acentricity of charge density which determines the macroscopic optical susceptibility of the third order [18]. It is well known that chalcogenides are very sensitive to external infrared laser irradiation, and the coherent light is of special interest. The illumination must be performed simultaneously by the fundamental and double frequency of the coherent beam (optical poling) which is formed by the generation of the second harmonic of the fundamental beam. Such treatment leads to the appearance of some spatial anisotropy even in amorphous glass, which is closely related to the optical effects of the described third-rank tensors which form the anisotropy of the medium by interacting with local energy levels [19]. For this reason, two coherent beams are used to form a grid in some broad range. Usually, this lattice is non-centrosymmetric and can cause additional laser-stimulated effects such as second harmonic generation, electro-optics and piezoelectricity.

Photoinduced piezoelectric properties were measured using a method similar to that described in [3], using a two-channel circuit with fundamental and double frequency beams falling at different incidence angles. A scheme for the investigation of coherent photoinduced changes is presented in Fig. 1.

The first ray passes through a nonlinear optical KTP single crystal cut at an angle of phase synchronism that doubles the frequency [20], and the second ray with the help of mirrors M1, M2, M3 and polarizers falls at a

Fig.1. Principle diagram for the investigation of coherent photoinduced changes by the method of optical poling.
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**Fig. 2.** The dependence of piezoelectric coefficients on the power density of bicolour irradiation by different laser wavelengths. The results are presented for optimal angles between two photoinduced laser beams.

CO\(_2\) corresponds to the fundamental photoinducing laser wavelength 10.6 \(\mu\)m; CO – 5.5 \(\mu\)m; Er:glass – 1540 nm; Nd:YAG – 1064 nm.

Certain angle on the photo-induced sample. The spatial control of piezoelectric properties was performed using an electrode tip of several \(\mu\)m diameters moving along the investigated sample. When illuminated by nanosecond and microsecond pulsed lasers (CO\(_2\), CO, Nd:YAG and Er:glass), the optimum incidence angle was 18-26°. The process of bicolor irradiation lasted from 2 to 3 minutes, and the measurements were made for the main probe beam for 10 s.

Metrological statistics were performed on more than 200 points of the surface. It was determined that irradiation by CO\(_2\) laser is essential for enhancing piezoelectric properties. The yield efficiency did not radically depend on the geometry of irradiation unlike Nd:YAG laser generating at 1064 nm. Treatment by Er:glass laser gives a result similar to that of Nd:YAG laser. For the case of CO\(_2\) laser, there was a greater contrast between the maxima and minima of piezoelectric changes, and for Nd:YAG and Er:glass lasers there are intermediate values of piezoelectricity. In this case, photoinduced piezoelectric changes have some nonhomogeneity region due to surface illumination. Photothermal effects did not exceed 5-7K.

The general view of photoinduced piezoelectric dependences at the laser power of 250, 300, 500 and 800 MW/cm\(^2\) is shown in Fig. 2. Optimal photo-induced changes were observed at a intensity ratio of fundamental and double frequency 50/50 for two-color irradiation. The optimum incidence angles for CO\(_2\) laser were 21-24°.

Fig. 2 shows that maximum piezoelectric changes were achieved with nanosecond CO\(_2\) laser illumination (10.6 \(\mu\)m). Observed increase was very significant, from 20 pm/V to 78 pm/V. The amplification process is not monotonous in comparison with pumping. At the beginning, \(d_{33}\) sharply increases with the power density up to 400 MW/cm\(^2\). The process is slower with further increase in power, coming onto saturation. This reflects the fact that, initially, the principal role belongs to the

The confirmation of the importance of photoexcited anharmonic resonances was obtained in the study of second harmonic generation in the Ag\(_{85}\text{In(Ga)\textsubscript{2}Si(Ge)S(Se)}\) crystals under irradiation of Er:glass, Nd:YAG and CO\(_2\) lasers [21]. The irradiation with CO\(_2\) laser yields higher SHG intensity compared to Er:glass and Nd:YAG lasers. As the principal mechanism responsible for the observed effect, we suggest an effective photoinduced excitation of the phonon subsystem after irradiation with CO\(_2\) laser, which confirms our results.

It is an important feature for applications that the continued treatment with laser power density up to 800 MW/cm\(^2\) does not cause photothermal destruction of
these materials.

**Conclusion**

Photoinduced piezoelectric properties of the \( \text{Ag}_2\text{In}(\text{Ga})_2\text{Si}(\text{Ge})_6\text{S}(\text{Se})_6 \) crystals were studied. It was established that the photo-excitation of anharmonic phonons is dominant in the case of irradiation by \( \text{CO}_2 \) and \( \text{CO} \) lasers, while the principal mechanism for irradiation by \( \text{Er:glass} \) and \( \text{Nd:YAG} \) lasers is the polarization of the electronic subsystem.

Observed effects are important not only for practical applications in laser semiconductor devices. They are also important for creating a common concept of complex chalcogenides to enhance their laser performance.

Performed research reveals new possibilities for using once synthesized chalcogenide material in different devices due to laser-controlled changes of corresponding optical constants. Our investigations show the ability to change the parameters of chalcogenides to a certain degree without the need for growing new crystals.

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[1] M. A. H. Muhammed, M. Döblinger, J. Rodríguez-Fernández, Switching, Journal of the American Chemical Society 137, 11666 (2015) (doi: 10.1021/jacs.5b05337).
[2] Z.L. Wang, Advanced Materials 24, 4632 (2012) (doi: 10.1002/adma.201104365).
[3] N. Narasimha Rao, I.V. Kityk, V. Ravi Kumar et. al., Journal of Non-Crystalline Solids 358, 702 (2012). (doi: 10.1016/j.jnoncrysol.2011.11.019).
[4] K. Ozga, A. Majchrowski, N. AlZayed et. al., Journal of Crystal Growth 344, 27 (2012) (doi: 10.1016/j.jcrysgro.2012.01.050).
[5] I.V. Kityk, O. Parasyuk, A.O. Fedorchuk et. al., Materials Research Bulletin 100, 131 (2018) (doi: 10.1016/j.materresbull.2017.12.013).
[6] A. Grachev, A. Kamshilin, Optics Express 13(21), 8565(2005) (doi: 10.1364/OPEX.13.008565).
[7] Yoon Myung, Hyung Soon Im, Chang Hyun Kim et. al., Chemical Communications 49, 187(2013) (doi: 10.1039/c2cc37513c).
[8] A.M. Andriesh, Semiconductors 32 (8), 867 (1998) (http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.501.9178&rep=rep1&type=pdf).
[9] I.V.Kityk, The Journal of Physical Chemistry B 107(B), 10083 (2003) (doi: 10.1021/jp030058a).
[10] Xue, V. Nazabal, M. Piasceki et. al., Materials Letters 73, 14 (2012), (doi: 10.1016/j.matlet.2011.12.089).
[11] A.S. Krymus, G.L. Myronchuk, O.V. Parasyuk et. al., Advanced Functional Materials 24(4), 521 (2017), (doi: 10.15407/fm24.04.521).
[12] B. Monserrat, E.A. Engel, Needs R. Physical Review B 92, 140302 (2015) (doi: 10.1103/PhysRevB.92.140302).
[13] I. Barchiy, M. Sabov, A. M. El-Naggar et. al., Journal of Materials Science: Materials in Electronics 27, 3901 (2016) (doi: 10.1007/s10854-015-4240-4).
[14] The TlInX₂–D₄VX₂ systems: phase equilibria and optoelectronic properties of solid solutions: a monograph/G.L. Myronchuk et. al. (Vezha-Druk, Lutsk, 2016).
[15] O.V. Parasyuk, G.L. Myronchuk, A.O. Fedorchuk, et. al., Crystals 6, 107 (2016) (doi: 10.3390/cryst6090107).
[16] V. Badikov, K. Mitin, F. Noack, et. al., Optical Materials 31(4), 590 (2009), (doi: 10.1016/j.optmat.2008.06.015).
[17] D.J. Knuteson, N.B. Singh, Kanner, A. et. al., Journal of Crystal Growth 312, 1114 (2010), (doi: 10.1016/j.jcrysgro.2009.10.051).
[18] G. Lemercier, C. Andraud, I.V. Kityk, et. al., Chemical Physics Letters 400, 19 (2004), (doi: 10.1016/j.cplett.2004.10.091).
[19] Y. Kogut, A. Fedorchuk, A. Zhbankov et. al., Journal of Alloys and Compounds 509, 4264 (2011) (doi: 10.1016/j.jallcom.2010.11.069).
[20] A.H. Reshak, I.V. Kityk, S. Auluck, The Journal of Physical Chemistry C 114, 16705 (2010) (doi: 10.1021/jp1072878).
[21] A.O. Fedorchuk, G.P. Gorgut, O.V. Parasyuk et. al., Journal of Physics and Chemistry of Solids 72, 1354 (2011) (doi: 10.1016/j.jpcs.2011.08.008).
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ІЧ-фотоіндуковані п'єзоелектричні ефекти у багатокомпонентних халькогенідах Ag$_2$In(Ga)$_2$Si(Ge)S(Se)$_6$

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Досліджено вплив зовнішнього опромінення лазерів CO$_2$, CO, Er: скла, Nd: YA на п'єзоелектричні властивості кристалів Ag$_2$In(Ga)$_2$Si(Ge)S(Se)$_6$. Максимальні фотоіндуковані зміни коефіцієнта п'єзоелектрики спостерігалися після опромінення CO$_2$ лазером. Фотоіндукційні двоколірні промені з довжиною хвилі 5,5 мкм викликають принаймні в 4 рази менший приріст п'єзоелектричних коефіцієнтів. Тому можна очікувати, що первинні механізми викликають збудження фононної підсистеми.

Ключові слова: халькогеніди, лазер, фотоіндуковані п'єзоелектричні властивості.