

Laser operated piezoelectricity in $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$ crystals

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Abstract Bicolour illumination by 1.54/0.77 μm 20 ns pulsed Er:glass laser beams leads to enhancement of the initial effective piezoelectric coefficients for $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$ crystals in a different way. The contribution of the photo-thermal effect did not exceed 4 %. The relaxation processes last up to 50 ms and are completely reversible with respect to piezoelectricity. The effect is reproducible even after more than 100 cycles of the photoinduced laser treatment. The use only of the monochromatic wavelengths 1.54 μm (0.77 μm) did not show sufficient enhancement of the effect, and the changes were commensurable with the background. The efficiency of the laser photoinduced treatment depends on the angle between the bicolour photoinducing beams, ratio of their intensities and their relaxation behaviour is a slightly different. However, at 50 ms the photoinduced piezoelectric signal disappears for the both samples. It is crucial that

laser polarizations of the photoinducing beams do not play important role.

1 Introduction

A search of IR optically operated chalcogenide materials presents a promising direction of modern optoelectronics [1, 2]. Among the chalcogenide materials very promising seem to be crystalline materials possessing both high polarizable Pb ions as well as silver cations. In the Ref. [3] it was reported novel quaternary chalcogenide $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeSe}_4$ crystals. These crystals possess non-centrosymmetric structure (space group $I-43d$) that indicates likely presence of effects described by third rank polar tensors (second harmonic generation (SHG), linear Pockels phenomenon, piezoelectricity etc.). We have observed earlier that the compounds $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$ (25 mol% substitution of Se for S) exhibit frequency-doubling effects such as SHG and two-photon absorption (TPA) [4, 5]. The crystals of the solid solution compositions with higher amount of selenium than 25–30 mol% cannot be easily grown by Bridgman–Stockbarger method due to the primary crystallization of PbSe which was shown in the Ref. [3].

In the present article we demonstrate an opportunity of use them as laser operated piezoelectric materials. This one presents a separate interest. The studies of the photoinduced piezoelectricity in the crystals cause recently an increasing attention [6, 7]. In the mentioned references it was observed a monotonous dependence of piezoelectricity versus the pump laser energy. In this work due to coexistence of two cations (Pb and Ag) one can expect an occurrence of nonlinear (non-monotonous) laser energy dependence with respect to piezoelectricity. Among the mechanisms defining the observed effect it should be point out the photoinduced

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polarizability, excitation of the anharmonic phonons, photoinduced space charge density acentricity [8–10].

In the previous works single (monochromatic) laser pulses were usually applied for the induction of piezoelectricity. In the present work we apply the bicolour coherent laser excitation which should cause the formation of some additional acentric gratings [11]. The use of bicolour laser excitations incident at different angles can form some local dc-electric field which enhance the materials polarizability. Additionally some roles here begin to play photothermal effect which is related to anharmonic phonons.

Such laser initiated dc-electric field may enhance the local charge density non-centrosymmetry defining efficiencies of the third rank polar tensors. As a consequence we have chosen a crystal which does not possess substantial piezoelectric effect during excitation by one (monochromatic) laser beam wavelength (fundamental or doubled frequency) and which requires bicolour formation of additional internal dc-electric field aligning the particular crystalline dipoles. After interruption of the illumination the crystal is relaxed to its initial state. These effects define the charge density acentricity. These effects are sensitive to the angles between the laser beams at different intensities.

2 Experimental

The growth of the single crystals with compositions $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$ up to 70 mm length and 10 mm diameter was reported in detail earlier [3, 4]. The experimental set-up for measurements of the photoinduced piezoelectricity versus photoinduced pump energy density is similar to the described in Ref. [12]. However, in the present work the photoexcitation was performed by two bicolour coherent beams of the 20 ns Er:glass laser with energy powers varied by Glan polarizer and pulse frequency repetition about 1 Hz. Additional monitoring of the scattering light was carried out using a ratio of intensities between the two mentioned beams. The latter was varied from 3:1 (fundamental/doubled frequency intensities) up to 6:1. Finally they were fitted following the maximally achieved piezoelectricity. These two beams were incident under the angles varying within the 10° – 57° . The control of the photoinduced grating was performed using diffraction of the one-mode He–Ne laser beam with power about 15 mW.

3 Results and discussion

Typically obtained space distributions of the photoinduced piezoelectricity (PIPE) are depicted in the Fig. 1. One can see that illumination by one monochromatic wavelength (Fig. 1a) do not give significant changes in piezoelectricity.

Following this figure one can see that there occur some sophisticated PIPE beam profile confirming a fact that only simultaneous use of two photoinducing bicolour coherent laser beams may favor enhanced dc-electric internal field defining an additional piezoelectricity.

In the Fig. 2 are presented behaviours of the effective piezoelectric coefficients for the two titled crystals versus photoinduced power energy density. Following the presented picture one can see that at relatively low energy densities (up to 0.7 J/cm^2) their energy laser behaviour is quite similar. There is observed also some narrow maxima (within 0.27 – 0.38 J/cm^2). However, with further enhancement of the bicolour photoinduced treatment energy the dependences become substantially different. For $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ containing samples the behaviour is saturated achieving piezoelectric magnitudes equal to about 1.6 – 1.7 pm/V . For the crystals ($\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$) the dependence shows essential decrease. Such difference may confirm principal role of the chalcogen anions which differently interact with the illumination.

So one can expect an occurrence of two different mechanisms for the titled crystals. Generally the presence of Se ions leads to some decrease of the effective energy gap from 1.79 up to 1.67 eV. Moreover, there occur also some trapping levels formed by intrinsic defects.

One can clearly see some additional bends in energy dependent piezoelectric behaviour versus the photoinduced power energy. The initial piezoelectricity is higher for the $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ crystals. However after applying of external laser field the general behaviour is almost opposite. For the sulphide there is observed a sharp jump of the piezoelectricity just at low photoinduced energy density (at

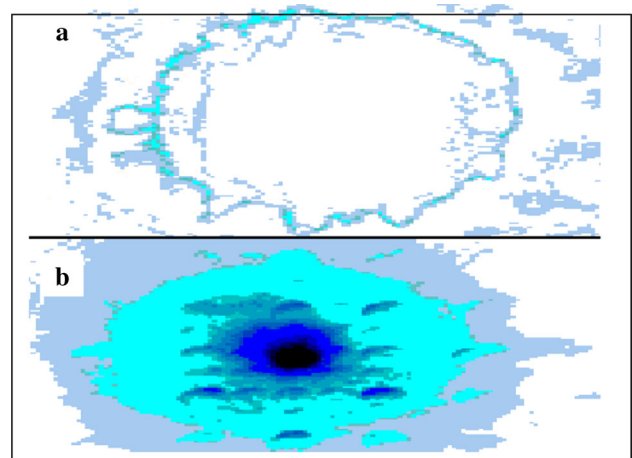


Fig. 1 Space distribution of the piezoelectric field changes after the illumination by one monochromatic wavelength (a) and after illumination by two bicolour coherent beams (b). The experiment was done both for the sample $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$ and the images are quite similar

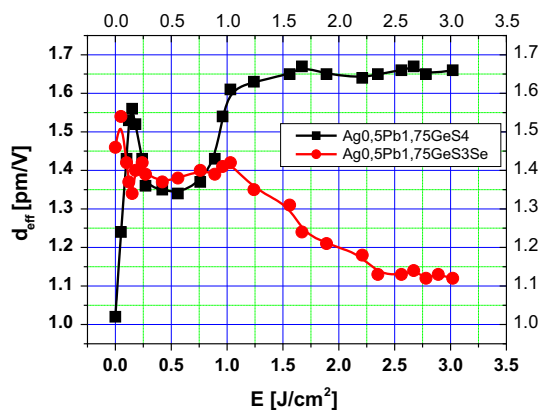


Fig. 2 Dependence of the photoinduced piezoelectricity of the titled crystals on the fundamental energy density of the photoinduced Er:glass laser. The picture corresponds to ratio 4:1 between fundamental and doubled frequency laser intensities

energy density 0.3 J/cm²). Afterwards it decreases slightly and begins to increase which reflects a competition between the photoinduced polarization and photo-thermal effects.

At the same time to find optimal (maximal photoinduced piezoelectricity (PIPE)) we have done the measurements at different angles between the photoinducing beams (see Fig. 3).

All the PIPE data are given in arbitrary units for convenience of readers. One can see almost symmetrical angle dependence for the both compounds. There exist clear maxima and they are shifted up to 7° for the two titled crystals.

To understand the origin of the effect, we have performed crystal-chemical and quantum-chemical simulations of the titled crystals using quantum chemical B3LYP DFT method for the particular structural fragments similarly to the described in the Ref. [13]. Crystallochemistry of the titled compounds consists of isolated tetrahedral

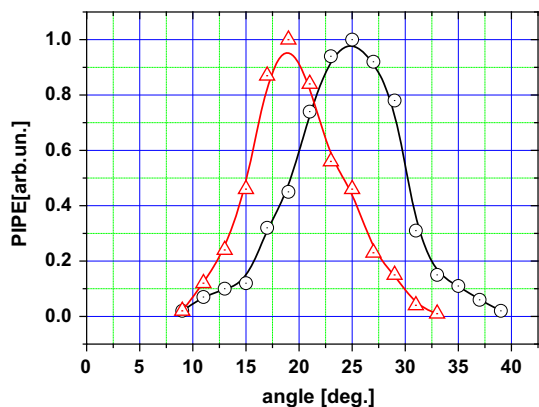


Fig. 3 Angle dependence of the PIPE for the two titled samples. Triangles—Ag_{0.5}Pb_{1.75}GeS₄; circles—Ag_{0.5}Pb_{1.75}GeS₃Se

tetrasulfido germinate anions [GeS₄]⁴⁻ and Ag⁺ (Pb₂₊) cations in the voids between the tetrahedra (see Figs. 4, 5). Following the performed photoinduced studies of GeS₄ clusters in such compounds principal role here may also play laser induced carriers [14]. Additionally the principal tetrahedral clusters are able to have photo-structural changes. Several photo-stimulated effects contribute to that phenomenon including photo-expansion, photo-darkening, and permanent self focusing. It appears also some light fluctuations [15].

An enhancement of the ground dipole moment for anionic atoms is possible by the isovalent substitution of S atoms with larger atoms, for instance Se due to higher pSe space delocalization. The principal role here belongs to the top of valence band which is formed prevalingly by p-chalcogen states.

After switching off of the external bicolor light the photoinduced piezoelectricity relaxes (see Fig. 6). It is interesting that despite the different behavior in time both compounds shows a completely reversible relaxation at about 50 ms. This fact may confirm the common features for the both compounds due to presence of long-range contribution of the principal tetrahedra.

It should be emphasized that the photoinduced temperature has changed not more than 4 K. The thermal control was performed immediately after swathing off of the external photoinduced light. Illumination by the single monochromatic laser beams did not give substantial changes of the effects. The role of the Ag ions is the same like for the photoinduced effects in other chalcogenide glasses [16].

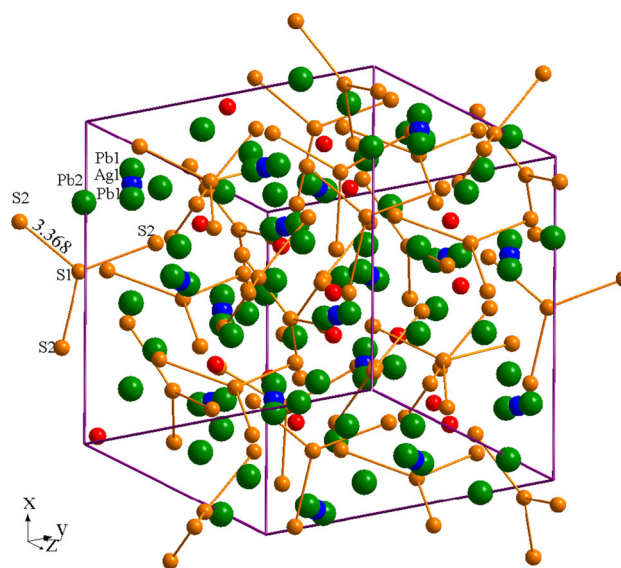


Fig. 4 General crystallochemistry of the Ag_{0.5}Pb_{1.75}GeS₄ structure

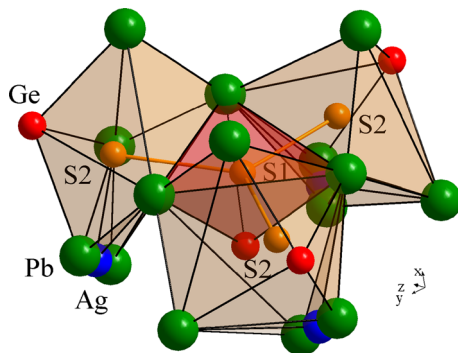


Fig. 5 Coordination of cations surrounding chalcogene atoms in the $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ structure. The performed calculation have shown that substitution of S by Se may enhance the ground state dipole moments from 6.7 up to 7.6 D

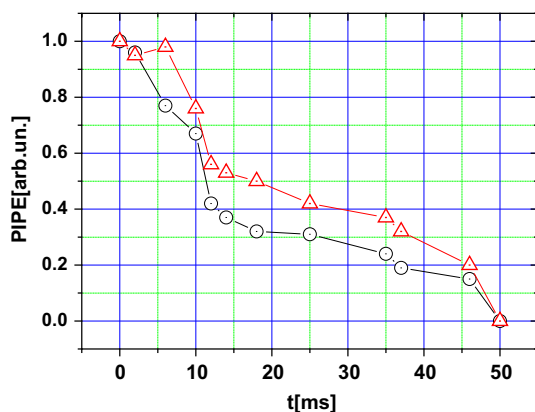


Fig. 6 Time decay of the PIPE after switching off of the external bicolour light. *Triangles*— $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$; *circles*— $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$

4 Conclusions

Quaternary chalcogenides $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ and $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeSe}_4$ single crystals have shown a huge potential for laser stimulated piezoelectric effects. A different dependence of the piezoelectric coefficients on external bicolour laser energy density was found. The initial piezoelectricity is higher for the sulphide crystals with respect to selenide. However, after applying of external bicolour laser field at wavelengths 1540/770 nm general laser power behaviour is almost opposite. For the sulphide compounds there is observed a substantial jump of the piezoelectricity just for the low photoinduced energy (about 0.3 J/cm^2). For the $\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_4$ containing samples the behaviour is saturated achieving piezoelectric magnitudes equal to about 1.6–1.7 pm/V. It is crucial that for crystals ($\text{Ag}_{0.5}\text{Pb}_{1.75}\text{GeS}_3\text{Se}$) the dependence shows essential decrease. Such difference may confirm principal role of the chalcogen anions which differently interact with the illumination. One

can see almost symmetrical angle dependence for the both compounds. There exist clear maxima and they are shifted by angles up to 7° for the two studied crystals. An enhancement of the ground state dipole moment for anionic atoms was achieved due to isovalent substitution of S atoms with larger atoms, for instance Se.

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