Evolution of a system of nonequilibrium acoustic phonons in monocrystalline and pure coarse-grained ZnSe

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Abstract. Propagation of nonequilibrium acoustic phonons in ZnSe single crystals grown by the free-growth process in the hydrogen atmosphere as well as in coarse-grained polycrystalline ZnSe grown by chemical synthesis from the vapor phase was investigated. The latter material is characterized by a microtwinned structure inside chaotically oriented grains. The measurements were carried out by the heat-pulse technique in the “transmission” geometry both by optical generation of phonons and by metal-heater generation. The characteristics of basic phonon scattering processes are estimated.

1. Introduction
Attention to the II–VI wide-band-gap compounds is caused by the use of these materials both for fabrication of effective ZnSe- and ZnSeS-based injection lasers operating in the blue and violet spectral regions and for development of spintronic devices based on ZnSe/GaAs heterostructures. ZnSe is also used as a cryostat window and as a substrate for many nanostructures. The fundamental problems in studying ZnSe are associated with the investigation of heat transfer and the determination of the effect exerted by point and extended defects on the mean free path of phonons in particular comparing monocrystalline and polycrystalline materials.

2. Experimental
ZnSe crystals were grown by the free growth method on an oriented single-crystal ZnSe substrate in a hydrogen atmosphere under the pressure of 0.45 bar at the growth temperature of 1190°C [1]. The samples for study were prepared in the form of 1.3-mm-thick plates with the (100) orientation. Polycrystalline ZnSe of 350 g in weight was synthesized at temperatures below 650°C from preliminarily purified components and was then subjected to homogenization and double vacuum sublimation at 900°C [2]. The condensate surface contained faceted crystals 50–200 μm in size with arbitrary growth directions. Figure 1 shows back scattered electrons (BSE) image of the same region of the sample measured by JEOL JSM-5910-LV microscope after etching for 1–3 min in 12.5% NaOH at 120°C. The presence of two simultaneously used detectors of back-scattered electrons make it possible to distinguish the contrast related to the variation of elemental composition and the internal structure (Fig. 1b) from the contrast caused by the surface relief (Fig. 1a). More fine structure is seen on Fig. 1b with a characteristic distance between the planes of 0.1–0.3 μm that is not revealed in the surface relief (Fig. 1a) and is not seen in the optical microscope. X-ray spectral microanalysis showed the absence of difference in the elemental composition of light and dark regions that proved the structural character of these inhomogeneities (twinning planes).
The propagation of nonequilibrium phonons was investigated in the transmission mode with the generation and detection of phonons on opposite sides of the sample. As a phonon generator, we used either the ZnSe surface excited by pulses from a nitrogen laser ($\lambda = 337$ nm, $\tau_p = 7.5$ ns) or a gold film evaporated onto the sample surface and heated by these pulses. Phonons were detected using a superconducting bolometer with an active region $50 \times 70 \mu m$ in size at the temperature of $\sim 1.7$ K.

![Image](image1.png)

**Figure 1.** BSE image of the surface of a coarse-grained ZnSe sample.

3. Results and discussion

3.1. Single crystal ZnSe.

The time-resolved responses of a bolometer to the arrival of nonequilibrium phonons under photoexcitation of the ZnSe surface are shown with circle in Fig. 2. The signal arriving at $t=0$ is optical in nature and is caused by photoluminescence reaching the bolometer, and then the arrival of longitudinal acoustic (LA) and transverse acoustic (TA) phonons is resolved.

The propagation of nonequilibrium phonons was analyzed using the results of the Monte Carlo simulation according to the model described in [3]. The basic processes involving nonequilibrium phonons in semiconductors at low temperatures are the spontaneous anharmonic decay and elastic scattering at point defects. These processes are characterized by the constants $A_{\text{LIFE}}$ and $A_{\text{SCAT}}$, which determine the mean times of phonons with respect to the decay ($\tau_{\text{LIFE}}$) and scattering ($\tau_{\text{SCAT}}$) as functions of the phonon frequency $\nu$: $\tau_{\text{SCAT}} = (A_{\text{SCAT}}\nu)\nu$ and $\tau_{\text{LIFE}} = (A_{\text{LIFE}}\nu)^{-1}$, respectively.

As in the case of CdTe and ZnTe [4], we assumed that phonon scattering by natural isotopes dominates because both zinc and selenium have several stable isotopes. In this case, the constant $A_{\text{SCAT}}$, which was calculated according to [5], is equal to $4.38 \times 10^{-41}$ s$^3$. To the best of our knowledge, there are no data on the constant $A_{\text{LIFE}}$ for ZnSe. The constant $A_{\text{LIFE}}$ for longitudinal acoustic phonons can be calculated according to the technique described in [6], which requires the knowledge of the second-order elastic modulus $C_{ik}$ and the third-order elastic modulus $C_{ijk}$. Owing to a large spread of the ZnSe elastic moduli data in literature [7], the constants $A_{\text{LIFE}}(\text{LA})$ calculated from these data lie in the range $(0.8-15.0) \times 10^{-54}$ s$^4$.

We simulated the propagation of nonequilibrium phonons in ZnSe with $A_{\text{LIFE}}(\text{LA})$ as a fitting parameter. The constant of spontaneous decay of fast transverse acoustic (FTA) phonons was assumed to be ten times less than the constant $A_{\text{LIFE}}(\text{LA})$, and the slow transverse acoustic (STA) phonons were considered to be nondecaying. In Fig. 2, the solid lines show the responses calculated for different values of $A_{\text{LIFE}}(\text{LA})$. The best agreement with experiment is achieved with the set of elastic moduli $C_{11} = 85.9$ GPa, $C_{12} = 50.6$ GPa, and $C_{44} = 40.6$ GPa and the constant $A_{\text{LIFE}}(\text{LA}) = 8 \times 10^{-54}$ s$^4$. The possible variations $A_{\text{LIFE}}(\text{FTA})$ introduce an error of about 10–20% in the value of $A_{\text{LIFE}}(\text{LA})$.

The responses detected during the generation of phonons with a gold film (Fig. 3) are also sufficiently narrow (curve 1) and broaden as the excitation level increases (curves 2, 3). This phenomenon is associated with the increase in the characteristic frequencies of phonons injected by the film into the sample and with the corresponding increase in the intensity of their scattering (the decrease in the
mean free path). With the excitation energy further increase the character of the responses changes (Fig. 3, curves 4–6). Specifically, a new smooth diffuse peak appears against the background of the ballistic peaks. The time of arrival of the maximum and its height increase as the excitation level increases. This behavior is typical of the formation of a region of local thermal equilibrium, a so-called “hot phonon spot”, in the material.

As can be seen, this peak appears at the pulse energy $E_P = 150–250$ nJ and the arrival time of the maximum at $E_P = 1100$ nJ reaches 1500 ns. The threshold energy of the hot spot formation was estimated in the framework the model proposed by Kazakovtsev and Levinson [8]. As a result, we obtained the threshold pulse energy required to form the hot spot (~80 nJ) and the spot lifetime (360 ns) at the energy $E_P = 1100$ nJ. These estimates and experimental data are of the same order.

Figure 2. Experimental bolometer response (circles) and calculated ones (solid lines) for $A_{\text{LIFE}}(\text{LA})= 15$ (1), 8 (2), and 0.8 (3) $\times 10^{-54}$ s$^4$.

Figure 3. Experimental bolometer responses with metal generator. Pulse energy: 35(1), 85 (2), 150 (3), 250 (4), 600 (5), and 1100 (6) nJ.

3.2. Coarse-grained ZnSe

Responses related to a polycrystalline ZnSe are much broader both for the gold-film heating and for photoexcitation (Fig. 4). This is caused by additional scattering by the grain boundaries and twinning planes. One should note that the duration of the responses for the case of gold-film heating increases (curves 1–4) with the laser pulse energy increase, i.e., with the film temperature; therewith the response shape begins to change at the pulse energies insufficient for the phonon “hot spot” formation. It means that the phonon free paths depend on frequency. Thus, in this case due to sample small thickness, the frequency-independent scattering of phonons at the extended defects does not dominate as it was previously observed in coarse-grained ZnTe [9]. The response duration under photoexcitation is even larger, since the more high-frequency phonons are generated.

In order to estimate the contributions of various microscopic phonon scattering processes we performed a computer simulation of phonon propagation in a medium consisting of individual blocks with account of elastic phonon scattering by block boundaries. In simulation, the lateral block sizes are taken to be 100 $\mu$m, according to the characteristic grain sizes. The dimension of the blocks along a normal to the sample surface is assumed to be 1 $\mu$m according to the average distance between twinning planes calculated from the SEM image taking into account the different twinning plane densities across the sample.

Figure 5 shows the responses calculated for various values of the probability of phonon scattering by twinning planes (solid curves) and the experimental response (circles). It is seen that the best fit is achieved if the probability of phonon scattering by twin boundaries is 3%. It should be noted that this estimate is qualitative, because the sample has a very inhomogeneous internal structure, with grains of various shapes and sizes and with various distances between twinning planes in grains.
4. Conclusion

Evolution of nonequilibrium acoustic phonon transport in ZnSe was investigated. The phonon "hot spot" – a local thermal equilibrium area – was identified. The hot spot threshold formation energy \( \sim 150-250 \) nJ (for the laser spot diameter \( \sim 0.1 \) mm) and lifetime up to 1500 ns was observed. For the first time the magnitude of anharmonic spontaneous decay of LA phonons was estimated \( \sim 8 \times 10^{-54} \) s\(^4\). Phonon transport measurements in coarse-grained ZnSe together with electron-microscopy data allowed us to establish the decisive effect of extended defects (twin plates) upon the phonon scattering. The probability of acoustic phonon scattering by twin planes was estimated. The estimation of phonon free paths \( \lambda \) without specifying the phonon scattering mechanisms for the polycrystalline ZnSe sample vary from 30 to 70 \( \mu \)m, that is less by an order than those for the monocrystalline ZnSe where they are about 400 \( \mu \)m.

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Figure 4. Experimental bolometer responses under photoexcitation (circles) and metal generator (solid curves 1–4) at pulse energy 2.5 (1), 5 (2), 10 (3), and 20 (4) nJ.

Figure 5. Experimental bolometer response (circles) with calculated ones for various values of the probability of phonon scattering by twinning planes: 1 (1), 3 (2), and 5 (3) %.