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INVESTIGATION OF HEAT TRANSFER OF BULK AND THIN-FILM PbInTe SAMPLES BY THE METHOD OF DYNAMIC GRATINGS

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Measurements of the thermal diffusivity of thin and bulk indium-doped lead telluride have been taken using a modified method of dynamic gratings. Thermal gratings were recorded by a 20 ns pulsed laser radiation at a wave length of 532 nm. Dynamic gratings were recorded by a 635 nm continuous laser radiation. The analysis of the diffraction signal kinetics made it possible to determine the life-time of thermal gratings recorded in the investigated samples. It is shown that the use of an additional homodyne field coherent with respect to the diffraction signal field makes it possible to enhance and filter off the selected information component. Based on registered kinetic dependences of the diffracted signal intensity, the thermal diffusivity of bulk and thin film indium-doped lead telluride samples was determined. It has been established that for a micron-thick film, the thermal diffusivity is ten percent lower than for a bulk sample. An investigation has been made into the dependence of the heat transfer in the said samples on their temperature and it has been shown that the rise in the samples' temperature in the range from 40 to 95^{o}C results in a 20-percent decrease of their thermal diffusivity.

Keywords: *thermoelectric material, lead telluride, heat transfer, thermal conductivity, thermal diffusivity, phase selection, thermal response.*

Introduction. Transport effects in PbTe-based thermoelectric materials have been actively investigated due to the promising outlook for the use of these materials in renewable energy technologies [1, 2]. In recent times, specialists′ attention has been drawn to indium-doped lead telluride [3], since it has a number of positive service properties.

This investigation deals with the thermal diffusivity of bulk and film polycrystalline lead telluride $Pb_{0.9995}In_{0.0005}Te$ samples. For the synthesis and preparation of bulk samples for investigation, use was made of the technology described in [3]. The subject of research was a 2-mm-thick disk cut out of a synthesized material with a surface polished to an optical quality. Film samples were produced from the same source material by vacuum evaporation [4, 5]. It is shown in [3] that the thermal conductivity of a bulk polycrystalline lead telluride sample is ~0.020 W/(cm·K) at a temperature 40–50^{o}C, which corresponds to a thermal diffusivity of 0.016 cm^2/s at a volumetric heat capacity of 1.24 J/(cm^3·K) typical of lead telluride. In [6], an investigation was conducted into a bulk PbTe single crystal, and it was established that its thermal diffusivity at room temperature is equal to 0.018 cm^2/s. In [7], the thermal diffusivity of a 5-μm-thick monocrystalline PbTe film grown on the surface of a BaF_2 monocrystal at room temperature was determined to be equal to 0.013 cm^2/s. The authors have explained this drop in the thermal diffusivity of PbTe by the high concentration of dislocations in the film (more than 10^8 cm^{-2}, according to electron microscopic control) due to the inconsistency of atom lattices of the substrate and the film and to the resulting high level of phonon scattering.

Surface-Type Thermal Dynamic Gratings. In this investigation, the thermal diffusivity of $Pb_{0.9995}In_{0.0005}Te$ samples was measured by the method of dynamic gratings (DG) which can be considered as an analog of the method of modulation spectroscopy [8–10] but in which the modulation of the material exciting power occurs in space rather than time. The method of dynamic gratings is based on writing a diffraction grating in a sample carried out due to thermooptical effects initiated on the sample surface by the interference field of two coherent light beams from a pulse laser in the absorption band of the sample material (Fig. 1). In a narrow-gap semiconductor, which lead telluride is, the absorption coefficient on a 532-nm-long excitation wave is approximated $0.5\cdot10^6$ cm^{-1} and hence, pulse heating occurs for a semiconductor surface layer with a thickness of about 20 nm. To form a diffraction signal and to detect it with a time resolution, the

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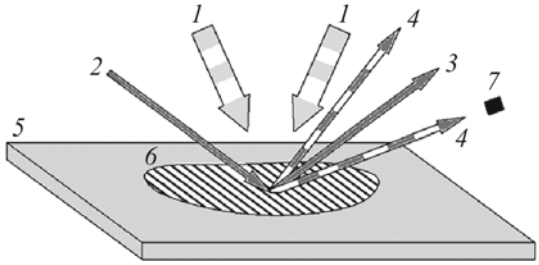


Fig. 1. Scheme of implementing the method of dynamic gratings: 1) coherent beams of pulse radiation creating a dynamic grating; 2) probing beam; 3 and 4) beams diffracted into zero and the first orders respectively; 5) sample; 6) dynamic grating; 7) photoreceiver.

635-nm radiation of a continuous laser was also directed into the zone of excitation of the sample material. A scheme of an experimental setup is given in [11], where an investigation was made into the heat transfer in films of lead telluride with an impurity of antimony and bismuth. The diffraction signal was registered in the reflection geometry. Then, the result of its photometry was used for calculating the sought parameter of the material.

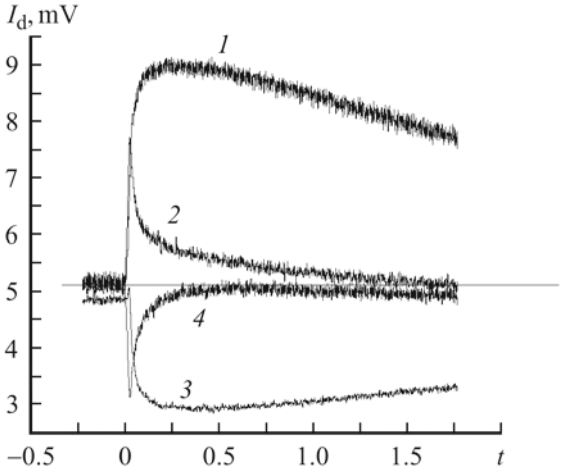
Registration of a Diffraction Signal in the Reflection Geometry. It is well known that the heating of an optical material as a result of it absorbing laser radiation leads to a change in its complex permittivity (complex dielectric constant) and to deformation of the material′s surface. In the case of a spatially modulated impact on the sample, several dynamic gratings of different physical nature are simultaneously formed in it, viz. phase and amplitude thermoreflection gratings and also a phase relief grating. In the case of this multiple response by the sample to a laser impact, to process experimental results, it is necessary to select one thermoresponse component allowing the most reliable determination of the sample′s thermal diffusivity. The solution of this problem within the framework of the method of dynamic gratings became possible due to the use of an additional light beam, viz., a homodyne beam that is collinear and coherent to the beam diffracted on the dynamic grating of the sample. Both beams are superimposed and interfere on the photoreceiver.

The selecting action of the homodyne field is implemented in the following way. In the simplest case of one exponentially decaying signal $E_d(t) = E_d(0) \exp\left(-\frac{t}{\tau}\right)$ and the constant homodyne field $E_b(t) = E_b$, the intensity on the detector $|E_d(t) + E_b(t)|^2$ is written in the form of a sum of three summands, two of which describe the decaying processes with the relaxation times $\tau/2$ and τ:

$$I_d(t) = I_b + I_d(0) \exp\left(-\frac{2t}{\tau}\right) + 2\sqrt{I_b I_d(0)} \exp\left(-\frac{t}{\tau}\right) \cos \Delta\varphi . \quad (1)$$

The amplitude of the sought signal described by the last summand in expression (1) depends on two parameters: the homodyne field and the phase difference between the two interacting fields. Furthermore, the phase difference $\Delta\varphi$ must be a controlled parameter. To identify one diffraction component and exclude an allied signal from consideration, it is necessary to register consecutively two kinetics of two interfering fields with the phase difference $\Delta\varphi = 0$ and π and then to subtract one kinetics from the other. The difference signal $I_{d1}(t) - I_{d2}(t) = 4^{\sqrt{I_b I_d(0)} \exp\left(-\frac{t}{\tau}\right)}$ makes it possible to identify and enhance the sought component of the diffracted signal with the relaxation time τ.

Formation of a Diffraction Response by a Surface Thermal Grating to a Laser Pulse Impact. Figure 2 shows diffraction signals for a 1.7-μm-thick $Pb_{0.9995}In_{0.0005}Te$ film on glass in assigning various phase differences between homodyne and diffraction fields. The presence of homodyne ensures selective selection and enhancement of diffraction signals of different physical nature. In the said figure, 1 and 3 reflect the kinetics of the process of diffraction of a probing beam on two phase gratings formed on the film surface due to the formation of a surface relief and a thermal change in the phase part of the complex refractive index in the thin near-surface layer of the film. This is evidenced by the presence of the initial stage of the sum diffraction signal buildup. Diffraction fields on relief-type gratings and a thermoreflection field, being present simultaneously, each decay under their own law and are in antiphase with respect to each other. The gradual increase of the diffraction signal in the initial part of kinetics 1 and 3 with a length of approximately 400–500 ns is the



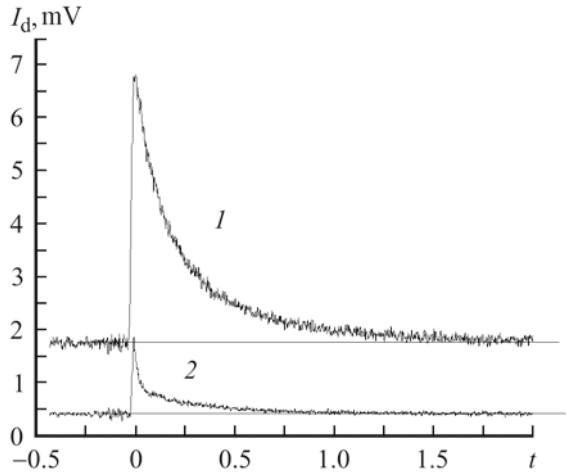


Fig. 2. Diffraction signals in a 1.7-μm-thick $Pb_{0.9995}In_{0.0005}Te$ film on glass with a grating with the period Λ = 12.5 μm at Δφ = 0 (1), π/2 (2), π (3), and 3/2 π (4): the horizontal line is the constant power of a homodyne beam.

Fig. 3. Diffraction signal decay kinetics in excitation–probing of the surface of a 1.7-μm-thick PbInTe film on glass from the air side (1) and from the substrate side (2).

result of decay of the phase surface thermoreflection grating. After its decay, we observe only one kinetics of the process of diffraction of the probing beam on a surface-relief type grating. Kinetics 2 is formed due to a thermoinduced change in the amplitude component of the complex dielectric constant on the film surface. This kinetics has been obtained in full under the same conditions as kinetics 1 except that the phase difference between the fields of diffraction and homodyne is set to be equal to π/2. This change in the kinetics of the process of diffraction of the probing beam (i.e., disappearance of its component 1 and the emergence of component 2) is due to the well-known phase shift of the diffraction field on the phase grating by π/2 with respect to the diffraction field on an amplitude-type grating. In this case, the homodyne and diffraction fields are inphased with respect to each other and, hence, they amplify the signal being registered. Kinetics 4 is the same kinetics as kinetics 2 but at the phase difference of the two fields Δφ = π/2 + π.

Figure 3 shows the kinetics of a diffracted signal for two variants of writing a dynamic grating in a PbInTe film. A homodyne field is absent. One can see that in recording the grating from the air side, the signal is higher than the signal obtained in recording the grating from the side of the glass substrate. This pattern can be due to the fact that in irradiating the sample from the side of the substrate, a dynamic grating is only formed due to a thermoinduced change in the complex dielectric constant on the film surface, since the film–glass contact prevents the formation of a surface relief. Thus, it can be said that the relatively low amplitude of diffraction on a surface thermoreflection dynamic grating and also the possibility of phase selection of the diffraction signal due to the use of a homodyne field are the factors that, in combination, can ensure the reliability of the obtained values of thermal diffusivity of a material.

Measuring Thermal Diffusivity of Bulk and Film Samples at Various Temperatures. The results of the described investigations have been used for a quantitative study of heat transfer in indium-doped lead telluride. Since, as shown above, the main role in the formation of a diffraction signal during sample irradiation from the side of the film is played by the surface–relief thermal grating, the time dependence of the height of the created relief is described by the relation [12]

$$H(t) = H(0)\ \mathrm{erfc}\ (\sqrt{t/\tau})\ , \qquad (2)$$

where erfc is an additional error function, $H(0)$ is the initial relief amplitude, and $\tau = \Lambda^2/4\pi^2\chi$. Relation (2) is only applicable in the case of the absorption of exciting radiation by the sample surface and when the velocities of heat transfer in the sample in the directions along the dynamic grating vector and along the normal to the sample surface are identical.

In accordance with foregoing, the procedure of determining the τ value included three actions: amplifying the diffraction signal from the phase grating by setting the phase difference of the homodyne and diffraction fields 0 and π, summation of the two registered kinetics, and the shift of the starting point from which we began to compare theory and experiment by 200 ns with respect to the laser pulse to minimize the contribution by the surface thermoreflection phase grating.

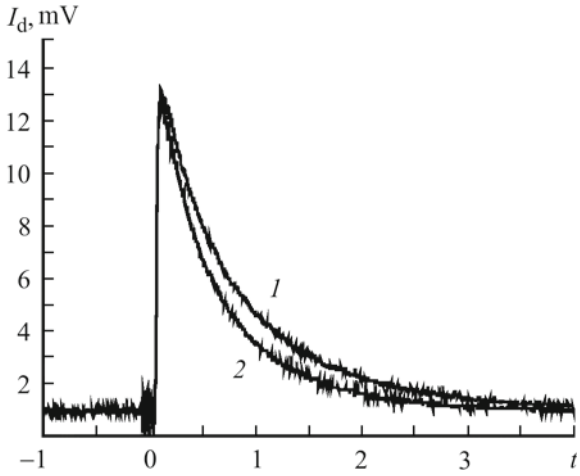


Fig. 4. Diffraction signal decay kinetics in a $Pb_{0.9995}In_{0.0005}Te$ bulk sample at the temperature T = 95 (1) and 40°C (2).

TABLE 1. Results of Measuring the Thermal Diffusivity of a Bulk $Pb_{0.9995}In_{0.0005}Te$ Sample and of a 1.7-μm-Thick Film of the Same Composition on Glass by Different Methods

Measurement method	T, °C		
	40	75	95
	χ, cm^2/s		
Parker method [3], bulk $Pb_{0.9995}In_{0.0005}Te$ sample	0.016	0.014	0.013
Method of dynamic gratings (Λ = 12.5 μm) bulk $Pb_{0.9995}In_{0.0005}Te$ sample	0.018	0.015	0.014
Method of dynamic gratings (Λ = 5 μm) $Pb_{0.9995}In_{0.0005}Te$ film on glass	0.016	0.013	0.013

Measuring the thermal diffusivity of the sample χ by the method of dynamic gratings yields its layer-thickness-averaged value $h = \Lambda/\pi$, since the heat released in the sample during the time of diffraction signal observation penetrates to this depth [12]. Testing a bulk $Pb_{0.9995}In_{0.0005}Te$ sample at dynamic grating periods of 25, 12.5, and 5 μm has shown that the thermal diffusivity of the sample material at a temperature of 40°C lies in the range of 0.018 $cm^2/s \pm 7\%$ and remains constant to the depth of at least h = 8 μm. This is indicative of the thermal homogeneity of the sample material along the normal to its surface.

A substantial factor in the work of PbTe-semiconductor-based thermoelectric materials is the dependence of their thermoelectric quality on the temperature T, in particular, due to the dependence of heat transfer parameters on temperature. Earlier, this circumstance was focused on in investigating bulk samples of compounds of lead telluride with indium $Pb_{1-x}In_xTe$ [3].

The investigation into the dependence of the thermal diffusivity $\chi(T)$ of bulk $Pb_{0.9995}In_{0.0005}Te$ samples was carried out at a dynamic grating period of 12.5 μm. Figure 4 shows two kinetics obtained at two temperatures of the sample, viz., 40 and 95°C. We can see an increase in the grating relaxation time as the temperature rises. The lifetime of the thermal grating

and the thermal diffusivity of the sample at the temperature $T = 40^{o}$C are $\tau = 2.18$ μs and $\chi = 1.80 \cdot 10^{-2}$ cm^2/s (kinetics 2), and at $T = 95^{o}$C, they are $\tau = 2.91$ μs and $\chi = 1.36 \cdot 10^{-2}$ cm^2/s (kinetics 1).

The results of measurements are summed up in Table 1. By way of comparison, it also shows the results of [3] obtained in investigating a similar bulk sample by the Parker method using an LFA 457 MicroFlash (Netzsch) device.

Conclusions. It has been experimentally established that the use of a homodyne field with a controlled phase and an intensity comparable with the intensity of a diffraction field makes it possible to select a diffraction component determined by the formation of a surface-relief phase grating making the highest contribution to the diffraction signal. Using the developed technique, it has been shown that increasing the temperature of the investigated bulk- and film-type samples in the range from 40 to 95^{o}C results in a twenty-percent decrease of their thermal diffusivity χ. It has been shown that there is a decrease of the χ value by about ten percent in transition from a bulk sample to a film one. The absence of mechanical contact with the investigated sample in the method being used is critically important for diagnostics of thin-film objects, which opens up broad prospects for its use in prompt access to information while synthesizing new film structures.

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NOTATION

I_d, diffraction intensity; I_b, homodyne field intensity; T, temperature; t, time; τ, dynamic grating lifetime; Δφ, phase difference between a diffracted field and a homodyne field; χ, thermal diffusivity. Subscripts: b, basic; d, diffraction.

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