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The Influence of γ-Irradiation on Thermoemf and Heat Conduction of $Ln_{0.01}Sn_{0.99}Se$ $(Ln - Pr, Tb, Er)$ Monocrystals

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ABSTRACT

Monocrystals are synthesized and grown according to Bridgman-Stockbarger method, and the influence of rare-earth elements (REE) as well as of γ-irradiation on electrophysical properties of $(SnSe)_{1-x}-(LnSe)_x$ $(Ln-Pr,Tb,Er)$ alloy system is investigated. During transition from SnSe to $(SnSe)_{1-x}-(LnSe)_x$ solid solutions, a partial compensation of charge carriers occurs and additional scattering centres appear. At low temperatures $T < 350$ K after irradiation with γ-quanta, thermoemf in samples of *p*-type conduction becomes higher and decreases in those of *n*-type conduction. In addition, under the influence of γ-rays radiation, defects come into being causing a decrease in lattice heat conduction and a rise in electron heat conduction. REE impurities are supposed to be positioned among the points of crystal lattice during irradiation with γ-quanta and, moreover, Frenkel defects are formed.

KEYWORDS

Thermoemf; Heat Conduction; Rare-Earth Elements (REE); Thermal Resistance; γ-Irradiation; Radiation-Induced Defects

1. Introduction

Interest to semiconductor compounds of A^4B^6 type is due to the promise of their use in semiconductor instrument making. So, for example, SnS and SnSe are employed as basic material for creating active elements operating in infrared region of optical spectrum and in thermodynamic converters [1,2], and for absorbing layer in thin film solar energy converters [3,4] as well as photoconductors [5], semiconductor sensors [6], microbatteries [7]. Over the last years, a great deal of effort has been put into the making of photo-voltaic instruments from economically advantageous low-toxic small-cost materials, the technology of manufacturing which is simple. Considerable promises in this respect have turned out to be semiconductor compounds of SnSe owing to low price of material which is explained by wide spread of tin and selenium in nature.

Semiconductor thermoelectric materials of A^4B^6 type with integration of rare-earth elements (REE) are of significant interest for researchers with the object of obtaining high-temperature thermoelectric converters. An investigation of potentialities of employing rare-earth elements for doping thermoelectric materials and obtaining highly efficient thermoelectric converters allows extending operating ranges towards high temperatures [8]. All converters, especially those functioning at elevated temperatures, are exposed to environmental effects: humidity, pressure, radiation etc. It has been demonstrated that physical parameters of materials containing REE are less exposed to external effects than other groups of semiconductor materials. The nature of chemical interaction between REE and various halcogenides is not the same.

However, their sulphides and selenides possess high mechanical strength and stability [9].

Of importance are the obtaining and complex investigation of physical properties and the effect of external factors, especially radiation on SnSe crystals doped with REE or solid solutions with small concentrations. The report [10] presents a complex investigation of interaction of SnSe-LnSe $(Ln - Pr, Tb, Er)$ systems using physico-chemical methods, contains a constitution diagram and informs the solubility of up to 3.5 mol percent at room temperature discovered on the base of SnSe. An incongruently melting triple compound of $LnSnSe_2$ type is formed in the system at the 1:1 ratio of the components. Physical properties of the obtained solid solutions and triple compounds are studied little. However, the radiation effects on them have not been examined.

The present report contains the results of investigating the effects of γ-irradiation on thermoemf and heat conduction of $Ln_{0.01}Sn_{0.99}Se$ $(Ln - Pr, Tb, Er)$ crystals. Radiation stability permits creating instruments on the base of these materials operating in conditions of high radiation background.

2. Method of the Experiment

Samples of $Ln_{0.01}Sn_{0.99}Se$ $(Ln - Pr, Tb, Er)$ were obtained through direct fusion of especially pure initial components in vacuumized quartz ampoules. The monocrystals were grown by way of oriented crystallization according to Bridgeman-Stockbarger method. Homogenizating annealing of the obtained single-phase samples was being carried out in the medium of spectrally pure argon for 5 days at 800 K. After the annealing samples of 2 × 4 × 18 mm in dimensions were cut from ingots of crystals on an electric spark unit. Some electro-physical properties of the obtained samples were investigated before and after irradiation over a wide range of temperatures (80 - 420 K).

The measuring of Hall effect and electric conduction of the initial samples and those doped with REE in the 80 - 420 K range was made according to standard compensation method in constant electric and electromagnetic fields [11]. The magnetic field of 11,000 oersted in strength is directed along [001] and electric current goes along [110]. Thermoemf and heat conduction were measured by stationary method in accordance with the procedure described in [12]. An isotope ^{60}Co with quantum energy of 1.25 MeV was used as a source. An irradiation dose was D = 65 Mrad.

3. Results and Discussion

Like basic substance SnSe, alloys of $(SnSe)_{0.99}$-$(LnSe)_{0.01}$ $(Ln - Pr, Tb, Er)$ system crystallize in orthorhombic syngonia (spatial group P_{cmn}, lattice parameters: $a = 4.46$; $b = 4.19$; $c = 11.57$ Å, elementary cell volume -216 Å^3). However, with increase in percentage of LnSe there occurs a rise in parameters of elementary cell density and microhardness and thermal effects relatively shift to the region of lower temperatures. A density value computed by roentgenography method is more for all samples than density determined from bottle method. It confirms that the obtained alloy system consists of vacancies of structural elements rich in defects.

Table 1 displays a number of kinetic parameters for $(SnSe)_{0.99}$-$(LnSe)_{0.01}$ $(Ln - Pr, Tb, Er)$ monocrystal at a temperature of 300 K: specific electric conduction (σ), Hall coefficient (R), thermoemf (α), thermal conductivity coefficient (χ), concentration of charge carriers (n) and Hall mobility which had been determined before and after irradiation. The table shows that the obtained solid solutions are partly compensated semiconductor materials.

With increase in percentage of LnSe in the composition α, σ and n decrease drastically, at $x \geq 0.005$ the sign of p-type conduction changes to that of n-type one $(SnSe)_{1-x}$-$(TbSe)_x$ and $(SnSe)_{1-x}$-$(ErSe)_x$ solid solutions. This fact is explained by the presence of structure vacancies in pure SnSe crystals—these vacancies create acceptor centres determining the type of conduction of material. The process of tin vacancy filling and the change in antistructure defects of selenium in $(SnSe)_{1-x}$-$(LnSe)_x$ solid solutions lead to a reduction in concentration of charge carriers and to a drop in an electric conduction value. A drastic decrease in electric conduction concentration and in concentration of charge carriers in the samples under study enables us to suppose that in the course of transition from SnSe to $(SnSe)_{1-x}$-$(LnSe)_x$ solid solutions a partial compensation of charge carriers takes place. With further increase in Ln content a gradual growth in n-type conduction is detected in $(SnSe)_{1-x}$-$(LnSe)_x$ solutions while activation energy of charge carriers goes down. The thermoemf coefficient of the crystals in the area of impurity conduction goes up at low temperatures and drops with the coming of intrinsic conduction which is characteristic of semiconductor compounds and solid solutions having sophisticated energy-band structure.

The fact of the change in the sign of charge carriers points to the event of compensation, a value of intrinsic concentration approaches that of impurity concentration and the degree of compensation produces a considerable effect on activation energy. It has been found that with the replacement of tin atoms by REE atoms in SnSe lattice the width of forbidden zone decreases. With increasing REE heat conduction in the solid solutions under study at low concentrations ($x \geq 0.005$) first diminishes

Table 1. Kinetic parameters T = 300 K.

Composition	Before irradiation						After irradiation					
	Type conduction	p(n) (10^{17} cm^{-3})	σ ($\Omega^{-1}\cdot cm^{-1}$)	μ ($cm^2V^{-1}c^{-1}$)	α (mkV·K^{-1})	χ (10^{-3} Vt·$cm^{-1}K^{-1}$)	Type conduction	p(n) (10^{17} cm^{-3})	σ ($\Omega^{-1}cm^{-1}$)	μ, ($cm^2V^{-1}\cdot c^{-1}$)	α, (mkV·K^{-1})	χ (10^{-3} Vt·$cm^{-1}K^{-1}$)
SnSe	p	7.0	16.13	144	+450	18	p	6.8	16.6	153	+465	17
$Pr_{0.01}Sn_{0.99}Se$	p	1.2	0.135	7	+498	17.2	p	0.98	0.19	12	+375	17.5
$Tb_{0.01}Sn_{0.99}Se$	n	0.83	0.006	0.45	−242	17.5	n	0.69	0.011	1	−290	15.7
$Er_{0.01}Sn_{0.99}Se$	n	0.45	0.058	8	−250	16	n	0.41	0.092	14	−280	15.8

by 15 percent, in case of further increase in REE content a rise in χ value is observed. Such change in heat conduction demonstrates that on the one hand, with the replacement of tin atoms by REE ones a partial recombination of vacancies with charge carriers occurs and at the same time additional scattering centres of charge carriers appear.

Figure 1 demonstrates temperature dependence of thermoemf (α) for $Ln_{0.01}Sn_{0.99}Se$ $(Ln - Pr, Tb, Er)$ monocrystals. As is seen, the $Pr_{0.01}Sn_{0.99}Se$ sample has p-type of conduction while the $Tb_{0.01}Sn_{0.99}Se$ and $Er_{0.01}Sn_{0.99}Se$ samples have n-type of conduction. After irradiation at a temperature of T = 77 K a thermoemf value in the $Pr_{0.01}Sn_{0.99}Se$ sample fell by 19 percent and has become respectively bay 25 percent and 60 percent more for the $Tb_{0.01}Sn_{0.99}Se$ and $Er_{0.01}Sn_{0.99}Se$ samples. At a temperature of $T = 300\,K$ occurs a decrease in a thermoemf value for the $Pr_{0.01}Sn_{0.99}Se$ sample by 10 percent while for the $Tb_{0.01}Sn_{0.99}Se$ and $Er_{0.01}Sn_{0.99}Se$ samples a rise respectively by 20 percent and 17 percent is observed. Relative change in thermoemf diminishes with increase in temperature.

Figure 2 gives temperature dependence of heat conduction for $Ln_{0.01}Sn_{0.99}Se$ $(Ln - Pr, Tb, Er)$ monocrystals. It is seen from this figure that with increase in temperature heat conduction of the samples under investigation goes down. A rise in heat conduction was caused by prolonged annealing of all samples. As was expected, an increase in the number of paramagnetic atoms of Pr, Tb, Er brought about a decline in heat conduction. A growth in the number of REE atoms in the composition leading to a decrease in heat conduction is related to nonregulability of crystallic structure of phonons and other scatterings on defects [8,9].

The heat in $Ln_{0.01}Sn_{0.99}Se$ $(Ln - Pr, Tb, Er)$ alloys is mainly transferred by phonons. Before irradiation electric heat conduction of the samples in the temperature range under study was between 7 and 12 percent of the total heat conduction and after irradiation of the samples with γ-rays the total heat conduction decreases. It demonstrates that along with the influence of γ-rays additional appearance of radiation effects is noted. Radiation effects are responsible for a decrease in lattice heat conduction and a rise in electronic heat conduction.

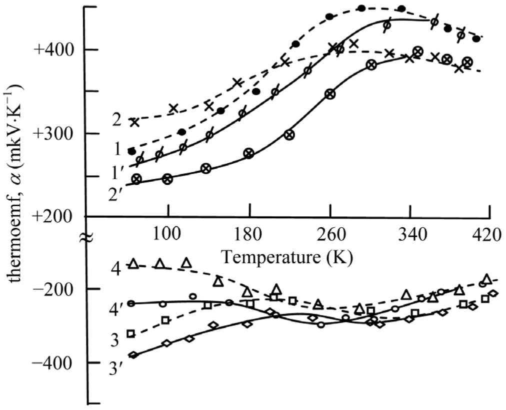

Figure 1. **Temperature dependence of thermoemf 1—SnSe; 2—$Pr_{0.01}Sn_{0.99}Se$; 3—$Tb_{0.01}Sn_{0.99}Se$; 4—$Er_{0.01}Sn_{0.99}Se$ (solid lines correspond to lines after irradiation).**

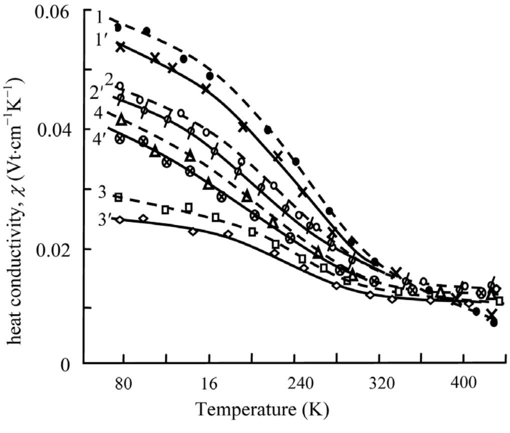

Figure 2. **Temperature dependence of heat conduction 1—SnSe; 2—$Pr_{0.01}Sn_{0.99}Se$; 3—$Tb_{0.01}Sn_{0.99}Se$; 4—$Er_{0.01}Sn_{0.99}Se$ (solid lines correspond to lines after irradiation).**

REE atoms are supposed to be positioned in vacant sites among the lattice points during irradiation of the samples and with localization self-compensation takes place together with the appearance of Frenkel defect. This brings about a drop in concentration of charge carriers, however, activation energy does not change, at high REE content in SnSe the concentration of charge carriers does not change very markedly. During γ-quanta irradiation, however, the formed radiation defects are partly compensated when interacting with structure defects. So, at a temperature of 330 K lattice heat conduction (χ_ℓ) of $\mathrm{Tb_{0.01}Sn_{0.99}Se}$ monocrystal became less by 8 percent while electronic heat conduction went up by 28 percent.

Temperature dependence of thermal resistance of the samples under investigation is illustrated in **Figure 3**. Temperature dependence of thermal resistance can be conventionally divided into two parts. In the first part which embraces the temperature range between 77 and 240 K thermal resistance *w* remaining linear in all samples changes parallelwise. The linear dependence of thermal resistance displays that it is mainly due to phonon-phonon interaction.

Irradiation is the cause of the appearance of defects in a crystal where vacancies, atoms in the interstitial site and various types of complexes are in interaction with one another and with chemical impurities. Radiation defects compensate themselves and conduction of semiconductors approaches intrinsic conduction [9]. Under the action of γ-rays in $\mathrm{Tb_{0.01}Sn_{0.99}Se}$ crystal having *n*-type of conduction compensation of donor impurity center takes place, radiation defects of acceptor type are created and at the expense of radiation defects mobility of charge carriers and electric conduction increase.

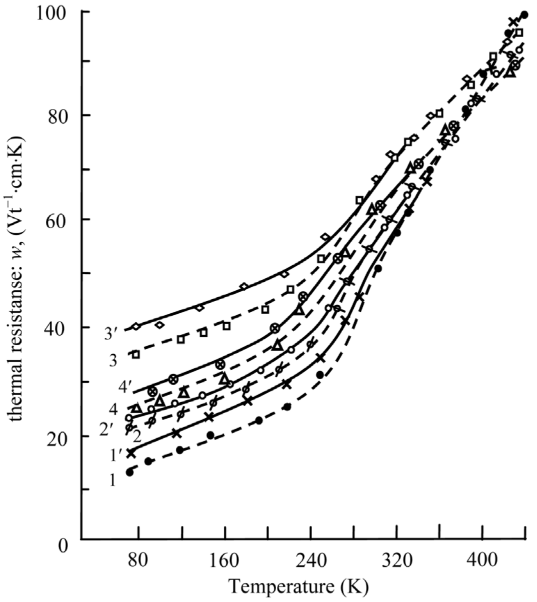

Figure 3. Temperature dependence of heat conduction 1—SnSe; 2—$\mathbf{Pr_{0.01}Sn_{0.99}Se}$; 3—$\mathbf{Tb_{0.01}Sn_{0.99}Se}$; 4—$\mathbf{Er_{0.01}Sn_{0.99}Se}$ (solid lines correspond to lines after irradiation).

4. Conclusion

During replacement of tin atoms by REE ones in $(\mathrm{SnSe})_{1-x}$-$(\mathrm{LnSe})_x$ alloys, a partial compensation occurs, and electric and heat conduction mechanisms improve due to a decrease in point defects. Comparative investigation of electrophysical and thermal properties of $\mathrm{Ln_{0.01}Sn_{0.99}Se}$ $(\mathrm{Ln-Pr,Tb,Er})$ monocrystals irradiated and non-irradiated with γ-rays demonstrates that electrophysical parameters change a good deal at low temperatures under the effect of irradiation with γ-quanta. With increasing temperature, relative change in thermoemf and heat conduction diminishes and totally disappears at $T \geq 350\ \mathrm{K}$. Radiation stability makes possible manufacturing instruments on the base of these materials operating in conditions of high radiation background.

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