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THERMAL CONDUCTIVITY OF $Pb_{1-x}Mn_xSe$ THIN FILMS

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Abstract: Thermal conductivity of $Pb_{1-x}Mn_xSe$ single crystal thin films has been studied at temperature range of $T=77\div 320$ K. Electron and lattice thermal conductivity have been determined according to the standard parabolic zone model and elastic scattering model of charge carriers. It has been established that general and lattice thermal conductivity decrease with temperature increasing. As well as, an increase in Mn amount in compositions causes a decrease in lattice thermal conductivity. And after annealing the general and lattice thermal conductivity increase. It has been determined that the transportation of thermal conductivity in $Pb_{1-x}Mn_xSe$ thin films is conducted mainly by phonons.

Keywords: epitaxial film, thermal conductivity, heat resistance, defects, impurity concentration.

1. Introduction

$A^{IV}B^{VI}$ group compounds and their solid solutions have been studied quite extensively [1,2]. The solid solutions formed on the base of these compounds are used in different types of energy transformations [1,3]. Recently, an interest to the obtain of their thin films by epitaxial method and their study has increased significantly [4]. The aim of the work is to obtain highly efficient, small-sized thin-filmed materials which can be used in electronics [3,4]. On the other hand, the obtain of semimagnetic magnetothermoelectric materials along with thermoelectric converters is of particular interest. The studied $Pb_{1-x}Mn_xSe$ solid solutions are of this type, as well.

0.01 and 0.04% thin films have been obtained from $Pb_{1-x}Mn_xSe$ solid solutions by epitaxial method and their thermal conductivity has been studied and analyzed before and after thermal treatment at the temperature range of $T=77\div 320K$ in the submitted article.

2. Experimental method and results

Thin films of the presynthesized $Pb_{1-x}Mn_xSe$ solid solutions containing $x=0,01$ and $x=0,04$ have been obtained by epitaxial method on BaF_2 substrates on device YBH71-П3 at 10^{-4} Pa vacuum. The thickness of the films has been in 3-5 microns and their stoichiometric compositions, crystal perfection have been tested by electron diffraction analysis and radiographic method. The morphology of their surfaces has been studied in the microscopy 09UOЭ-100-005. C-0000 lead, crystal selenium purified with a special method and electrolytic manganese have been used in obtaining the studied solid solutions. In order to create homogeneity in the obtained samples, they have been kept downwards in a heater with the temperature of 420K in argon medium for 72 hours. After that, physical-chemical analysis has been carried out and crystal perfection has been checked. The samples are of p-type conductivity. Their thermal conductivity and heat resistance have been measured and determined within the range of $T=77\div 320K$ and then, kept in argon medium at the temperature of $T=720K$ for $t=240$ hours. General thermal conductivity of the samples has been remeasured and calculated, proper graphs have been plotted and analyzed. The measurements have been carried out in absolute stationary mode, using the built-in heater by the compensation method [5-7]. In order to control the accuracy of the measurements, as a benchmark

it has been used p-PbSe crystal which has been checked and of which geometric dimensions, except its thickness, are close to the sizes of thin films. Geometric dimensions of p-PbSe crystal have been $(2 \times 6)20\text{mm}^3$. The measurements have been conducted in comparison with the standard crystal under the same conditions. Differential copper-constantan thermopairs of which cross-section is $\Phi=0,11$ mm have been used during the measurements. A standard sample has been placed in the device, vacuum in $\sim 10^{-4}\text{Pa}$ order has been created and its thermal conductivity has been determined by establishing $\Delta T=4\div 6$ degrees temperature difference along the sample. In order to reduce partly the heat loss it has been used a screening core. For affixing thermopairs to the sample it has been used a special solder. Thermopairs have been passed through special holes which are on the main heater and affixed to the sample. Potentiometer P 308 and direct current circuit have been used within the measurements. After measuring the standard sample, the thin films to be studied have been placed in the device without changing the condition and parameters of used sources and appropriate experiments have been carried out. In this case, the geometrical dimensions of thin films except for thickness have been close to the benchmark.

The silt with the examples has been affixed to a special asbestos-cement pillow by means of БФ2 technical glue and placed in the above-shown core. The temperature gradient formed in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ crystals has been $\Delta T \approx 4\div 6$. The literature [5-7] has been used for carrying out the experiments. The errors made within the measurements have been in 5,6% order.

Graphs have been plotted based on the data obtained from the experiment and analyzed. Temperature dependence of general thermal conductivity (χ_0) of the samples is given in figure 1a. As it is seen from the graphs, the general thermal conductivity of the three samples decreases proportionately with temperature increase. At the given temperature compared to χ_0 belonging to PbSe there is a decrease in the value of χ_0 with increase of Mn amount in its Mn element-doped compounds. For example, at 90 K temperature the decrease in the sample containing $x=0,01$ is 14%, but in the sample containing $x=0,04$ is 29% (figure 1a and 1b).

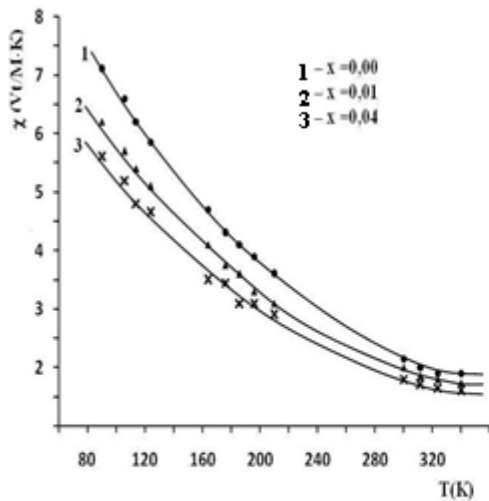


Fig. 1a.
Temperature dependence of general thermal conductivity in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ epitaxial films.

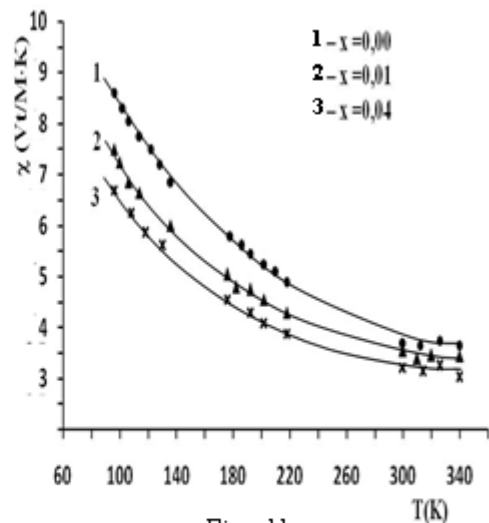


Fig. 1b.
Temperature dependence of general thermal conductivity after annealing in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ epitaxial films.

In order to investigate the influence of annealing on defective nature of the compounds, their lattice (χ_l) and electron (χ_{el}) thermal conductivity have been calculated. In order to calculate the electron thermal conductivity, it has been used electric conductivity (σ) of the samples obtained from the experiment and thermoelectric power (α) [8,9]. It has been established that the general

thermal conductivity χ_0 consists of mainly lattice (χ_l) and electron (χ_{el}) thermal conductivity at the studied 77÷320 K temperature range [5-8] and calculated using the following formula.

$$\chi_0 = \chi_l + \chi_{el} \quad (1)$$

For this purpose, agreeing with the fact of degenerate and elastic scattering of charge carriers, electronic thermal conductivity for the usual parabolic zone has been defined as

$$\chi_{el} = L\sigma T$$

applying Wiedemann-Franz law [8]. Here, $L = A \left(\frac{k_B}{e} \right)^2$ is the Lorenz number. Charge carriers are likely to be scattered from acoustic lattice oscillations and the value of A has been determined from $A = f(\alpha)$ dependence and $L = 4,03 \cdot 10^{-8} \left(\frac{V}{K} \right)^2$ for PbSe crystal [7,8]. The general thermal conductivity coefficient for PbSe crystal film corresponds to the value specified in the literature [9] within the experimental error. The values of electronic thermal conductivity of the samples without annealing for compounds at 90K temperature are given in the table below.

Table. $T=90K$

Compositions	$\sigma, \text{Om}^{-1}\text{cm}^{-1}$	$\chi_l \cdot 10^{-3}, \text{Vt/cm} \cdot \text{K}$	$\chi_{el} \cdot 10^{-3}, \text{Vt/cm} \cdot \text{K}$	$\chi_{el}, \%$
x=0,00	672	72,1	0,41	0,6
x=0,01	210	62,3	0,12	0,2
x=0,04	1370	56,2	0,81	1,5

Values obtained from experience show that, the increase of Mn - concentration in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ system leads to a decrease of χ_0 , as well as χ_l - thermal conductivity. The reason of this is the formation of additional heat resistance due to phonon scattering by additional phonons.

$\omega(T)$ dependence of heat resistance of three samples at the temperature $T=77\div 320K$ directly confirms this result in the graphs of 2a and 2b (figure 2). As it is seen from the graph, $\omega(T)$ dependence changes linearly up to $T \leq 310K$ and it shows the occurrence of heat resistance in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ crystals due to phonon-phonon scattering. The increase of values of χ_0 and χ_l after annealing is explained by the decrease of scattering of point (vacant) defects and the increase of frequency of phonon oscillation [5,9].

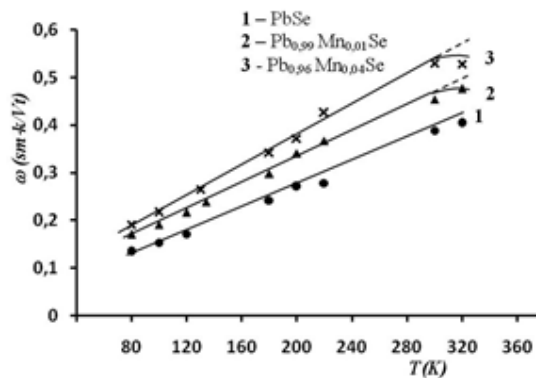


Fig. 2a.
Temperature dependence of heat resistance in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ epitaxial films

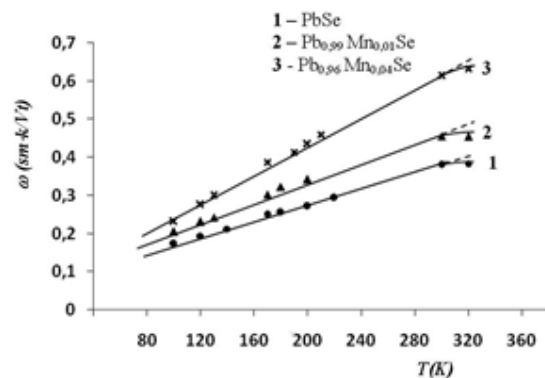


Fig. 2b.
Temperature dependence of heat resistance after annealing in $\text{Pb}_{1-x}\text{Mn}_x\text{Se}$ epitaxial films

As we mentioned, χ_0 and χ_1 decrease depending on the amount of Mn in compositions, but annealing increases the value of both parameters. The samples after annealing differ from previous samples with structure defects (lead vacancies). Therefore it can be accepted that, [9,10]

$$\frac{1}{\chi'_q} = \frac{1}{\chi_q} + \frac{1}{\chi_d} + \frac{1}{\chi_{ion}} \quad (3)$$

Here, χ'_1 and χ_1 are lattice thermal conductivity before annealing and after annealing at the temperature $T=720$. The sum of $\frac{1}{\chi_d} + \frac{1}{\chi_{ion}}$ characterizes the additional scattering of point defect centers of phonons. It has been used Clemens formula to estimate the amount of total defects in crystals [11]. In the samples, the concentration of defects (N_d) is defined as:

$$N_d = \frac{0,9h^2G}{12\pi^2TV_0S^2} \quad (4)$$

according to Clemens formula. Here, V_0 is elementary lattice volume, v - rate of sound, G - the number of defects in the elementary lattice of samples, S – scattering parameters and it is generally accepted as one [11], T – absolute temperature.

At 80K temperature, lattice constants of the samples for slightly deformed cubic lattice [10] are $a=6,1105$, for $x=0,01$ – containing samples - $6,1008\text{\AA}$; for $x=0,04$ samples - $a=6,1005\text{\AA}$. Elementary volume V_0 has been calculated by using these values. The rate of sound in the samples is expressed with the expression of $v = \sqrt{\frac{E}{\rho}}$ and $E = 10,8 \times 10^{10}$ is Pa-Jung module, $\rho = 8,16 \frac{g}{cm^3}$ - density [12]. The dependence of lattice thermal conductivity on the concentration of structure defects for the samples at $T=80K$ temperature has been given in the figure 3. Calculations show that, the concentration of defects increases by the increase of amount of Mn element and this leads to a decrease of lattice thermal conductivity. As it is seen from the graph, on the other side, χ_1 thermal conductivity for the given samples increases after annealing. And it shows the effect of annealing on structure defects. In other words, annealing decreases structure defects and partially restores normal oscillation of phonon (N-process) [13,14].

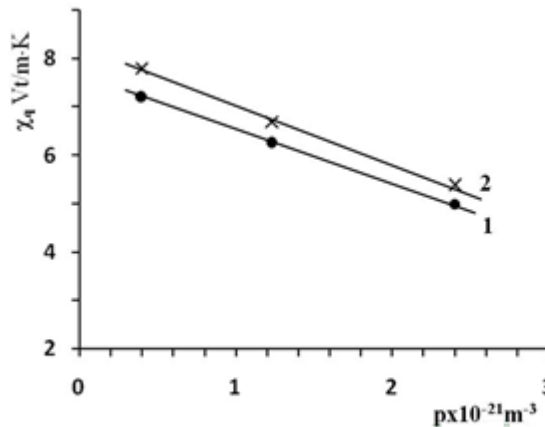


Fig. 3. Concentration dependence of lattice thermal conductivity in $Pb_{1-x}Mn_xSe$. $T=90K$. 2-after annealing

If we agree that, Mn^{2+} and Pb^{2+} take part as bivalent in the compositions and consider their ion radiuses being 0,91 and 1,26 Å, then the increase of amount of Mn increases weak violation of oscillation of crystal lattice and leads to a change of periodic potential in the crystal. As a result, crystallochemical sizes of ions will change [11]. In its turn, annealing restore regular and continuous crystalline structure and it leads to an increase of thermal conductivity of samples.

So, it has been determined as a result of research that, lattice thermal conductivity takes main part in films of $Pb_{1-x}Mn_xSe$ monocrystals obtained epitaxial method. As it is seen from the table, electron thermal conductivity is small enough in the obtained compositions and annealing process changes heat resistance of lattice vacancy, accordingly [9].

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ТЕПЛОПРОВОДИМОСТЬ ТОНКИХ ПЛЕНОК $Pb_{1-x}Mn_xSe$

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Резюме: Исследована теплопроводность тонких пленок монокристаллов $Pb_{1-x}Mn_xSe$ в температурном интервале $T=77\div 320K$. Определена электронная и решеточная теплопроводность в соответствии со стандартной параболической зонной моделью и моделью упругого рассеяния

носителей заряда. Установлено, что общая и решеточная теплопроводность уменьшаются с ростом температуры. Кроме того, увеличение количества Mn в композициях вызывает уменьшение решеточной теплопроводности. А после отжига повышается общая и решеточная теплопроводность. Установлено, что перенос теплопроводности в тонких пленках $Pb_{1-x}Mn_xSe$ осуществляется в основном фононами.

Ключевые слова: эпитаксиальная пленка, теплопроводность, термостойкость, дефекты, концентрация примесей

$Pb_{1-x}Mn_xSe$ NAZİK TƏBƏQƏLƏRİNİN İSTİLİKKEÇİRİCİLİYİ

R.S. Mədətov, H.R. Nuriyev, Ş.S. İsmayılov, R.M. Məmişova

Xülasə: $Pb_{1-x}Mn_xSe$ monokristallik nazik təbəqələrinin $T=77\div 320$ K temperatur intervalında istilikkeçiriciliyi tədqiq olunmuşdur. Standart parabolik zona modelinə və yükdaşıyıcıların elastiki səpilmə modelinə əsasən elektron və qəfəs istilikkeçiriciliyi təyin olunmuşdur. Müəyyən edilmişdir ki, temperaturun artması ilə ümumi və qəfəs istilikkeçiriciliyi azalır. Tərkiblərdə Mn-nin miqdarının artması da qəfəs istilikkeçiriciliyinin azalmasına səbəb olur. Dəmləmədən sonra isə ümumi və qəfəs istilikkeçiriciliyi artır. Müəyyən olunmuşdur ki, $Pb_{1-x}Mn_xSe$ nazik təbəqələrində istilikkeçiriciliyinin daşınması əsasən fononlar hesabına baş verir.

Açar sözlər: epitaksial təbəqə, istilikkeçiriciliyi, istilik müqaviməti, defektlər, aşqar konsentrasiyası.