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LIMITING POSSIBILITIES FOR REDUCING THERMOELECTRIC MATERIAL – METAL CONTACT RESISTANCE

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The theoretical aspects of evaluating the electrical resistance of thermoelectric leg – metal contact are considered. A physical model of such a contact and methods for calculating the main components of the contact resistivity, namely the resistivity of the interfacial layer and the resistivity related to the transfer of charge carriers through a potential barrier at the boundary between a material of the thermoelectric leg and a metal, are proposed. The contact resistivity for thermoelectric legs made of Bi_2Te_3 based materials with deposited antidiffusion nickel layer is calculated. It was established that the contact resistivity in such thermoelements reaches the value from $0.25\cdot10^{-6}$ to $2.5\cdot10^{-6}$ Ohm×cm^2 and depends on temperature and interfacial layer thickness. The value of boundary resistivity due to a potential barrier in such legs varies with temperature from $0.5\cdot10^{-7}$ to $2.5\cdot10^{-7}$ Ohm·cm^2. It was shown that boundary resistance can be reduced by increasing the doping carrier concentration in the ultra-thin layer of thermoelectric material near the nickel contact. It was established that increasing the concentration of doping impurities in the near-contact zone by one order of magnitude with respect to its optimal value results in decreasing the electrical boundary resistance by two orders. Under these conditions, the boundary resistivity approaches the minimum possible value and is 10^{-9} Ohm·cm^2. It is demonstrated, that the findings are in good agreement with the known experimental values of contact resistivity.

THERMOELECTRIC POTENTIAL OF SUPERLATTICES DESCRIBED BY THE FIVAZ MODEL

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Layered semiconductor materials, including thermoelectric, are prone to the formation of superlattices. The simplest, but common and effective model for describing the band spectrum of such superlattices is the Fivaz model. In this model, the motion of charge carriers in the plane of layers is described by the effective mass method and perpendicular to the layers - by the tight binding method. The thermoelectric potential of such superlattices is revealed when the vectors of the temperature gradient and the electric current density lie in the plane of layers. They can be used effectively, if the Fermi energy of two-dimensional gas of charge carriers with a quadratic law of dispersion in them at the absolute zero temperature is greater than or comparable to the width of a narrow miniband, which describes the motion of charge carriers in the direction perpendicular to the layers. The corresponding ratio can be considered the degree of nonparabolicity of the band spectrum. In this case, at certain material parameters, namely, the effective mass of electron in the plane of layers $m^* = m_0$, carrier concentration $n_0 = 3\cdot10^{16}$ cm^{-3},

narrow miniband width $\Delta = 2.16 \cdot 10^{-4}$ eV, distance between the layers $a = 30$nm in the temperature range of 300-500 K one can achieve the generator efficiency 37.5%, which is very close to the Carnot cycle efficiency. At present, material with such parameters has not been created, although there is no fundamental physical law or principle that would prohibit its creation. At the same time, with increasing distance between the layers or increasing the width of the miniband, the thermoelectric efficiency of such material decreases rapidly. It is due to these factors that even bismuth telluride can also be considered as superlattice, but with a low degree of nonparabolicity, and, consequently, relatively low thermoelectric efficiency due to the significant width of the allowed band.

Another important direction of using superlattices in thermoelectricity is the creation of heterocontact structures on their basis, which make it possible to achieve low contact resistance values when creating thermoelectric energy converters, which is very important for miniaturization of thermoelectric devices. This is achieved due to the fact that, as a result of effective blocking of the scattering of charge carriers in the direction perpendicular to the layers, the resistivity of material decreases drastically, approaching at high degrees of nonparabolicity of the band spectrum of material the resistivity of metal. Our calculations, as well as the experiments of other authors, show that in this way it is possible to reduce the electrical contact resistance "thermoelectric material-metal" up to 10^{-9} Ohm·cm^2, i.e. to the so-called "detection limit".

Finally, in superlattice thermoelectric materials with a high degree of their nonparabolicity, it is possible to achieve a difference in the Seebeck coefficients in the plane of layers and perpendicular to them up to 300 μV / K. And this is important for creation of anisotropic thermoelements and other thermoelectric devices using thermoEMF anisotropy, in particular, eddy thermoelements. An important advantage of anisotropic thermoelectric devices as compared to thermocouples is that they do not require a complex thermoelement connection system.

MULTISCALE MODELING OF UNSTEADY NON-EQUILLIBRIUM BOLTZMANN TRANSPORT EQUATION

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The thermoelectric materials could complement the renewable energy extraction from sources like solar energy and it can also act as an alternative to heat engines while harvesting waste heat from several electrical devices like computers. The figure of merit ZT is responsible for the thermal efficiency of TE materials which can be increased by decreasing the lattice thermal conductivity of the materials. It has been found that ZT is enhanced in nanostructured grains with small misorientations. It has also been observed that nanocomposites such as optimally doped Bi2Te3 and its solid solution with Sb2Te3, Bi2Se3 and silica powder can enhance ZT. These grains and nanoinclusions are of nanometer to micrometer sizes for which first principle calculations and molecular dynamics based calculations become computationally too expensive to even attempt. Therefore, not only there is a need to understand thermal transport across interfaces, grain boundaries and naoninclusions using known methods, but a mutiscale modeling of Boltzmann Transport Equation (BTE) will also help understand thermal and electrical transport across all these defects and composites involving several scales. We aim to develop a multiscale framework in which the phonon information coming from molecular dynamics/DFT simulations will be coupled with finite element methods for solving BTE which has advantages such as constructing a well defined boundary solution to be used to study thermal transport across the grain boundaries or phase and interface boundaries for nanoinclusions. This will be cross verified by the experiments involving nano-composites of $Bi_x Sb_{2-x}Te_3$. The finite volume scheme is already in use but the current work uses FEM whose accuracy could be improved by mesh refinement or by increasing the order of interpolation functions.

EFFECTIVE MEDIUM THEORY FOR THE THERMOELECTRIC PROPERTIES OF COMPOSITE MATERIALS WITH VARIOUS PERCOLATION THRESHOLDS

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Modified effective medium theory is constructed for calculating the effective properties of thermoelectric composites with different values of percolation thresholds. It is shown that even at concentrations beyond the critical region, the threshold value is essential for determining the effective properties. Two fundamentally different cases of a set of local properties of the composite are considered. In one of these cases, the conductivity and thermal conductivity of one of the phases is simultaneously greater than the conductivity and thermal conductivity of the other phase. The second, anomalous case, when the electrical conductivity of the first phase is greater than that of the second, but the thermal conductivity of the first phase is less than that of the second, shows unusual concentration behavior of effective conductivity, i.e. with an increase in the well-conducting phase, the effective conductivity shows a decrease (rather than growth as in the standard case), which at goes over to growth.

A NEW DT-FGTM APPROACH IN THERMOELECTRIC ENERGY CONVERSION

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Typical commercial modules are constructed using uniform semiconductors with carrier concentration optimized for the assumed temperatures of heat sink Tc and heat source Th. To enhance the efficiency of thermoelectric conversion, the concepts of segmented (i.e., composed of different materials) or functionally graded thermoelectric materials (FGTM), with carrier concentration adjusted to the temperature gradient, are used. A new extended concept of Double Tuned Functionally Graded Thermoelectric Material (DT-FGTM) is proposed. This approach assumes the simultaneous tuning of two electronic parameters, i.e., the bandgap Eg and the Fermi level EF to gain a high averaged figure of merit ZTave over the operational temperature range. Additionally, the resonance effect in PbTe and adjust EF with selected donor and acceptor impurities is utilized. It was shown that within the developed DT-FGTM approach, high efficiency in energy conversion of at least 15 % could be achieved. Co-doping PbTe with resonance elements (In and Tl) significantly improves the homogeneity of the Seebeck coefficient distribution along the thermoelectric leg due to the stabilization of EF position. Moreover, in the specific case of In the harmful process of In diffusion into the PbTe matrix could be reduced, which can extensively prolong the service time of the TE generator.

2. METROLOGY IN THERMOELECTRICITY

METROLOGY OF THERMOELECTRIC MATERIALS

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It is well-known that no significant improvements in the quality of thermoelectric materials have been achieved over the past decades. The best materials that are used in thermoelectric energy converters for generator and refrigeration technology are bismuth compounds, such as Bi - Te, Pb - Te, Ge - Si and, sometimes, others.

Various methods are used to find new materials and improve known ones. The chemical composition is changed, various impurities are introduced, materials of different structures: heterogeneous, nanostructures, powder and others are used. The influence of these effects on the material is determined experimentally by measuring electrical conductivity σ, thermoEMF α, thermal conductivity κ and figure of merit Z.

The analysis of the conventional methods and equipment for measuring the properties of thermoelectric materials has shown that measurement errors can really cause the lack of progress in increasing the thermoelectric figure of merit Z. The largest errors occur when determining the figure of merit by measuring electrical conductivity, thermoEMF and thermal conductivity on different samples. Thus, the errors in determining the Seebeck coefficient are at the level of 2 to 5% (two-probe and four-probe methods), electrical conductivity at 2 to 3% (two-probe method, four-probe method), thermal conductivity at 3 to 7% (relative method, Angström method, laser flash method). Therefore, the total error in determining the figure of merit can reach 20%. In addition, since the material is nearly always somewhat heterogeneous, this causes an additional error, which averages to 3 to 5%. The total error in determining Z in this case can reach up 23 to 25%. Such errors become an obstacle in solving problems of increasing the figure of merit of the material, since the measurement accuracy may be lower than the improvement in the properties of the material when the factors affecting it change.

The most reliable results can be obtained with the absolute method and the Harman method used. A series of studies carried out at the Institute of Thermoelectricity has shown that the errors in determining the figure of merit by the Harman method can be at the level of 5 to 6% in a number of cases only, when a multitude of additional parameters is known, such as: the emissive properties of the sample and thermostat, thermal conductivity of current leads and thermocouples, etc.

The absolute method is more effective as it allows minimizing the majority of sources of errors in an instrument. It is widely used in the creation of standards and has important advantages, namely: measurements of σ, α, κ, Z are performed simultaneously on one sample, which reduces errors; small samples can be used for measurement; thermoelectric parameters are found from classical formulas with no corrections applied.

The results of studies of the effect of various factors on the accuracy of measuring the thermoelectric properties of materials by the absolute method are presented. New methods have been developed to minimize errors, such as gradient radiation screens with special radiation rings, glittering reflector on a thermostat, heat locks, metal contact structures for reliable connection of the end surfaces of the sample with current and thermal contacts. The achieved error values: thermal conductivity is 2.4%, electrical conductivity is 0.7, thermoEMF is 0.8, and figure of merit is 4.7%.

Using methods to reduce errors, an automated measuring device was manufactured to determine the parameters of thermoelectric materials in the temperature range of 30 to 500 ° C. The combination of the above measures makes it possible to reduce the errors in determining the figure of merit by 3 to 5 times. To study high-temperature materials, a modification of the measuring unit was developed, which allows measurements in the temperature range from 30 to 900 ºC. Methods have also been worked out to significantly increase the speed of measurements by up to 5 t.

TEMPERATURE MEASUREMENT PROBLEMS IN THE ROTARY FRICTION WELDING PROCESS

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Точне визначення температури зони процесу набуває все більш важливої ролі в процесі контролю і моніторингу ротаційного зварювання тертям. У даний час вимірювання температури здійснюється за допомогою вбудованого в інструмент датчика температури (зазвичай термопари). Оскільки їх не можна прикріпити безпосередньо до області з'єднання, розсіювання тепла всередині інструменту і в навколишнє середовище викликає відхилення в вимірах, а також затримку вимірювання температури в часі. У статті описаний процес і пов'язані з ним проблеми, як пряме вимірювання температури в ході процесу може бути досягнуто за рахунок використання термоелектричного ефекту між інструментом і робочою деталлю, без заміни інструменту шляхом введення додаткових датчиків температури.

THERMOMETRY: FROM THE THERMOCOUPLE TO THE HIGH-RELIABILITY THERMOELECTRIC SMART SENSOR

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The analysis of sources of instability of metrological and operational characteristics of thermocouples is carried out, which showed that in stressed thermoelectrodes the density of heat and electric current flows depends not only on the temperature and electric potential gradient, but also on the mechanical stress gradient. This causes the dependence of thermometric parameters of thermoelectric materials on the value and nature of mechanical stresses that occur in them during operation. The possibility and expediency of achieving high metrological reliability of modern thermoelectric sensors due to the involvement of smart technologies and due to the use of nanoscale elements that do not have plastic deformation components is shown.

METROLOGICAL ASSURANCE OF THE PRODUCTION OF THERMOELECTRIC CONVERTERS

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Depending on the place of application in the measurement process, the methods of improving the accuracy of measurements are divided into 2 groups. These are methods of improving the accuracy of the measuring instrument and methods of improving the accuracy of measurement results. The fundamental difference between them is as follows. The object of the 1st group is the stabilization of conversion function. The object of the 2nd group of methods is the stabilization of the output signal of the tool. Hence the two types of influence on the conversion function of 3B (thermoelectric converter): The 1st group of methods involves the internal influence on the conversion function, i.e. correction. Whereas the second group includes the impact on the indicators of 3B by amending.

3. THERMOELECTRIC MATERIAL SCIENCE

CHEMICAL BONDING AND THERMOELECTRIC BEHAVIOUR OF MATERIALS

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Substantial information sources for the development of materials are the composition-crystal structure-properties relationships and diagrams. For thermoelectrics, such diagram is multidimensional with complex interplay of its components. In general, the phenomenon of thermoelectricity is thought to be well understood from the physical point of view. Different chemical aspects of thermoelectric behavior like lone pairs, Van-der-Waals bonds, valence band convergence etc. are still under consideration [1-5]. Chemical bonding understood as a system of physical forces within a chemical entity creates a natural bridge between chemical and physical properties of materials. Recent systematic quantum chemical studies show that atomic interactions play a key role in the chemical and structural organization of thermoelectric materials. On the one hand, bonding forms the basis for the total electron balance in the material regulating electron concentration and transport (electron engineering). On the other hand, atomic interactions influence the heat transport in the materials as well (phonon engineering). Spatial distribution of regions with different types of chemical bonding – bonding inhomogeneity and anisotropy - influences especially the thermal transport more than other crystallographic only features [6]. Quantum chemical bonding indicators in real space help to find electronic counts necessary to stabilize structural pattern with a band structure with a (pseudo)gap and a strong DOS gradient at the Fermi level [7-9], and at the same time to understand the reasons for appearance of special features in the real structure defining e.g. mechanical properties of thermoelectrics [10].

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PHASE BOUNDARY MAPPING TO ENGINEER DOPANT DEFECTS

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We often understand the physical properties of Zintl Phases by considering the perfect crystalline material that is defect free. Yet this perfect, stoichiometric (valence balanced) crystal is an intrinsic semiconductor with equal number of electrons and holes. To make a n-type or p-type semiconductor we typically use point defects to introduce a slight valence imbalance that leads to excess electrons or holes. Often intrinsic defects such as vacancies, interstials or antisite defects, provide the necessary carriers to make the material a good thermoelectric (e.g. Zn4Sb3, Bi2Te3-Sb2Te3, YbxCoSb3, etc.). Most materials, however, require extrinsic dopants to be a good thermoelectric and intrinsic defects only make it more complicated. Sometimes intrinsic defects are so prevalent they are killer defects that prevent any dopant from making the material n-type or p-type. By understanding that atomic chemical potentials influence defect energy and also define regions in phase diagrams we can use phase boundary mapping to explore all the possible thermodynamic defect states of a material to avoid killer defects. The most dramatic demonstration of this is the discovery of high zT n-type Mg3Sb2 which only occurs in Mg-rich Mg3Sb2 where Mg-vacancies are suppressed. Point defects can also make gradual but profound changes to the band structure compared to the defect free compound. This includes increasing band gap for higher temperature application, reducing conductivity mass for higher mobility or band convergence for dramatic increase in density of states (Pb(Se,Te), Mg2(Si,Sn), Bi2Te3-Sb2Te3,). In principle all of these defects can be better controlled by engineering chemical potentials through phase boundaries. Even the Ni content MNiSn (M = Ti, Zr, Hf) Half-Heusler thermoelectrics can be sufficiently altered to make substantial differences in electronic properties. The excess Ni produces impurity states in the band gap that changes the effective band gap and leads to additional electron and phonon scattering.

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THERMOELECTRIC PROPERTIES OF BISMUTH THIN FILMS AND BISMUTH-ANTIMONY SOLID SOLUTION

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The bismuth-antimony solid solution is known as the most effective low-temperature (temperatures below 200 K) thermoelectric material. At the same time, last works show the possibility of using quantum and classical size effects in electronic phenomena, as well as internal deformations to increase the thermoelectric efficiency of materials. In our work we study the possibilities of increasing thermoelectric efficiency of thin bismuth films and bismuth-antimony solid solution using the above approaches.

Bismuth films with a thickness from 10 nm to 1 μm and bismuth-antimony films with an antimony concentration from 3 to 15 at. % Sb. Plates of monocrystalline mica (muscovite) and a polyamide film were used as substrates. The coefficient of thermal linear expansion (CTE) of these materials is 8 * 10-6 K-1 and 45 * 10-6 K-1, respectively. Bismuth CTE in the trigonal plane is 10.5 * 10−6 K − 1. Thus, mica substrates cause in-plane tensile deformation, and polyimide substrates cause in-plane compression deformation of the film at temperatures below the film formation temperature. With the help of several developed original techniques for producing thin films, the quality of their structure was varied: from fine-crystalline, with block sizes of the order of the film thickness to a monocrystal structure. The control of the film structure was carried out by atomic force and electron microscopy and X-ray structural analysis.

The temperature dependences of the resistivity and thermoelectric power were investigated by the method that excludes the occurrence of deformation in the film-substrate system, and the thermoelectric power factor was calculated in the temperature range 77-300K. It has been found that for bismuth-antimony films to obtain the maximum thermoelectric power, the ratio of the crystallite size and film thickness is critically important, which is due to the different confinement of electrons and holes by the surface and crystallite boundaries. For bismuth films on mica, with the thickness less than 30 nm, with a decrease in thickness, an increase in the absolute values of the thermopower occurs at low temperatures, which is apparently due to a change in the electronic energy spectrum due to the quantum size effect. We did not find this effect for bismuth-antimony films, apparently due to the lower annealing efficiency for thin films of the bismuth-antimony solid solution and, as a result, the smaller values of charge carriers' coherence length in comparison with pure bismuth films, large values of which are critically important for observing coherent phenomena. It was found that the use of films on substrates with a high temperature expansion leads to a decrease in the thermoelectric power, especially in the low-temperature region. The maximum thermoelectric power and power factor correspond to thick block films of Bi0.88Sb0.12 on mica. In these films, the maximum power factor of 4*mW / K^2m was obtained at temperatures 200-250 K.

The study of ultrathin monocrystal bismuth-antimony films with minimal defectiveness and high surface perfection seems promising for achieving high values of thermoelectric power, which provides a long coherence length of charge carriers with a predominance of specular reflection from the film surfaces.

However, at the moment, the technology for creating such films has not been developed in the world.

NANODOT EFFECTS FOR THERMOELECTRICS: FROM THEORETICAL PREDICTIONS TO OBSERVATIONS

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Nanoscale effects favor the thermoelectric (TE) efficiency in multiple ways. They are maximized in structures of nanodots where quantum confinement is ultimate and scattering enhanced. Thus, possibilities of optimizing electron and phonon transport emerge. Developing nanostructures with optimized TE properties has been proven extremely challenging. The research is being boosted by the continuous progress of the fabrication and measurement technology. We will report on advances of the last years in the observation and modelling of thermoelectric effects in nanostructures of nanodots that we had previously predicted theoretically and are now getting increasing interest in the fields of thermoelectricity and nanoscale heat management.

RESENT DEVELOPMENTS IN THERMOELECTRIC HEUSLER ALLOYS

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Semiconducting Heusler alloys have been sintered for the first time in 1970 [1] but the first studies of electronic band structure and transport properties were performed 20 years later [2]. Until now the most intensively studied semiconducting Heusler alloys are n-type MNiSn-based compound (M = Ti, Zr, Hf) with C1b structure (so-called half Heusler alloys) which have been considered as perspective thermoelectric materials for applications at temperatures $T \geq 700$ K, thanks to a large thermoelectric figure of merit $ZT > 1$.

Recent studies of FeRSb-based compounds (R = V, Nb) have shown that the sigh of the Seebeck coefficient in these compounds is very sensitive to doping [3] This made it possible to achieve the record for p-type half Heusler thermoelectrics ZT above 1 in FeNbSb-based materials [4,5].

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POLAR INTERMETALLICS AND THERMOELECTRICITY

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In this lecture, the avenement of polar intermetallics (often referred as Zintl Phases) into the field of thermoelectricity will be narrated.

From the famous 14-1-11 to the more obscure, but very common, 1-2-2 structure type, from exploratory research to technological development, Zintl phases are now regarded with deep scrutiny. This rich and ever expanding family of compounds shines by its variety of structure types combined with exhilarating physical properties. This is there story.

POSSIBILITIES OF INCREASING THE EFFICIENCY WITH PERMEABLE THERMOELEMENTS

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The results of studies on promising applications of permeable thermoelements are presented. The results of computer simulation of various variants of permeable thermoelements (porous, planar, segmented, etc.) in the modes of electric energy generation and thermoelectric cooling are given. Using the methods of the mathematical theory of optimal control and computer design, multifactor optimization problems have been solved and structural and thermophysical parameters have been determined that provide the maximum values of energy conversion efficiency.

The results of computer calculations indicate the possibility of increasing the coefficient of performance by 20-50% in comparison with traditional thermoelectric cooling. In the mode of electrical energy generation, the use of permeable thermoelements makes it possible to obtain 1.1-1.5 times higher energy efficiency compared to traditional thermoelements.

Samples of permeable planar thermopiles of materials based on Bi-Te-Se-Sb have been obtained. The experimental data confirm the main propositions of the theory and indicate the possibilities of a wider application of thermoelectricity.

INFLUENCE OF INTERLAYER INTERACTION ON THE PROPERTIES OF DOPED BISMUTH TELLURIDE

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Anomalies in the temperature dependence of the crystal lattice parameters and kinetic parameters of bismuth telluride doped with copper and indium Bi2Te3 <In, Cu> are explained by changes in the chemical bond and the effect of defect centers.

The redistribution of the electron density between the metal and the central chalcogen layer in the five-layer stack of the crystal framework, at a certain temperature range, leads to a negative thermal coefficient of linear expansion. The polarity of the covalent bond and the decrease in the Bi-Te (2) interatomic distances are directly affected by the magnitude of the interlayer interaction. The energy of thermal motion when approaching the value of the energy of interlayer interaction leads to deviation of bonds and to fluctuations in the distribution of electron density in the bulk of the crystal.

MULTILAYERS OF SELENIUM DOPED BISMUTH TELLURIDE COMPOUND FOR THERMOELECTRIC APPLICATIONS

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Technological advancement needs development of modes and methods for harvesting of waste Heat through thermoelectric devices. Telluride compounds are very good thermoelectricity generating materials. These have shown excellent thermoelectric properties in the temperature range 50°C - 200°C. Recent reports indicate that their multilayer designs will have better thermoelectric properties. In this report preparation and characterisation of alternate multilayer thin films of Bismuth telluride (Bi_2Te_3) and Selenium doped Bismuth telluride ($Bi_2Te_2.7Se_{0.3}$) have been reviewed and reported. Results show that good quality multilayer films have been grown.

DIRECT MEASUREMENT OF THE PELTIER EFFECT ON A GRADED-GAP CRYSTAL OF BI100-X-SBX SYSTEM WITH CURRENT FLOW ALONG ITS CLEAVAGE PLANE IN THE RANGE OF COMPOSITION VALUES 7.5<X<11.5 AT%

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Earlier, one of the authors of this work experimentally discovered and theoretically substantiated the phenomenon of polarity of a number of kinetic properties on graded-gap crystals of the *Bi-Sb* system in a transverse magnetic field [1-4]. In [5], the authors presented the experimentally discovered and theoretically substantiated phenomenon of the dependence of thermal conductivity on the mutual direction of the gradient of the band gap and the temperature gradient in the investigated crystalline image of a given solid solution, including outside the magnetic field. The essence of this previously unknown phenomenon is that the specific thermal conductivity changes significantly in magnitude when the direction of the temperature gradient changes with respect to the direction of the gradient of the band gap of the semiconductor sample (the inhomogeneity of the composition and temperature are directed along the length of the sample either co-directionally or counter-directionally).

In this work, we present an experimental result obtained on a Peltier couple, in which the *n*-leg is a crystal of a solid solution of the Bi-Sb system in the form of a rectangular parallelepiped of length a = 8 mm, width b = 2.6 mm and thickness c = 1.3mm, the cleavage plane is parallel to the directions of length and thickness. The current is directed along the length of the *n*-leg. The composition gradient (monotonic change in the concentration of antimony) is also directed along the length of the *n*-leg crystal. A graph of the change in the concentration of antimony along a single-crystal ingot of a Bi-Sb solid solution is shown, where the dots indicate the values of its concentration obtained by the X-ray luminescence analysis method, the graph line was obtained by the spline interpolation method from the measured points. The sample is cut from a section of this ingot from the value of the longitudinal coordinate along its length equal to 18 mm to the value of the coordinate 26 mm, the length of the sample is directed along the ingot and the crystal cleavage plane. Monocrystalline ingot is obtained by a combination of zone and normal crystallization from seed. Thus, at one end of the *n*-leg, we have an antimony concentration of approximately C1≈7.5 at%, and at the opposite end of approximately C2≈11.5 at%. In accordance with the data [5] at the temperatures of the measurement (the temperature of the thermostat on which the Peltier couple is mounted has a value of T≈100K). The band gap at the first end is ΔE1 0 (there is a slight overlap of the valence and conduction bands), and at the second end ΔE2≈15 meV, that is, the band gap increases monotonically when moving from the first to the second end of the sample (in the linear approximation of the movement of the bands). This circumstance means that the sample (*n*-leg) is a graded-gap semiconductor crystal. As the *p*-leg of the Peltier thermoelement, a thin copper plate with geometry close to optimal in relation to the above-described *n*-leg is used. The temperature of the thermostat on which the Peltier couple is mounted, and the temperature of the cooled contact of the investigated Peltier thermoelement were measured using copper-constantan thermocouples. The thermostat, equipped with automatic thermal stabilization, together with the investigated thermoelement attached to it, is located in a sealed evacuated vacuum chamber immersed in boiling nitrogen.

In conclusion, it should be noted that the crystallographic orientation of the *Bi-Sb* crystal used in the experiment is not the most optimal from the point of view of the Peltier cooling efficiency, both in terms of thermoelectric power and thermal conductivity. Orientation is significantly more effective when the direction of the current and temperature gradient in the legs of Bi-Sb crystals are parallel to their trigonal axis, but we have not yet succeeded in growing a monotonically inhomogeneous crystal with the direction of the composition gradient parallel to the trigonal axis (perpendicular to the cleavage plane).

It is also important to note that until now the effect of polarity in graded-gap (gradient-inhomogeneous) crystals of the *Bi-Sb* system was predicted and experimentally confirmed by the author of this work for all kinetic parameters important for thermoelectricity, except for the Peltier effect. This work is a kind of research result, important for the practical use of the polarity effect during Peltier cooling.

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TOPOLOGICAL INSULATORS AND THERMOELECTRICITY

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Topological insulators (TIs) represent a relatively recently discovered new class of objects of solid state physics [1]. TIs are insulators with metallic conduction in the surface layer due to strong spin-orbit interaction; electronic states are characterized by the Dirac dispersion law and topologically are protected against backscattering at non-magnetic impurities and defects. The protection of topological surface states has been extensively studied, and their existence has already been confirmed. However, until now, significantly fewer experimental data have been reported on the peculiarities of the transport properties of TIs caused by their special band structure.

It turned out that most TIs belong to the best thermoelectric (TE) materials (Bi_2Te_3, Bi_2Se_3, Sb_2Te_3, etc.), and recently a number of works have appeared, in which the authors explain this fact from various points of view. Understanding of this phenomenon could make it possible to use the presence of the Dirac surface layer to increase the TE figure of merit Z, that is, to develop fundamentally new methods for increasing Z through the use of topological properties.

The most promising in this respect is the use of thin films, in which the role of the surface layer in conduction increases in comparison with bulk crystals, because with decreasing film thickness, the relative contribution of the surface states to the kinetic coefficients increases.

Several works dealing with possible effects of topological surface states on the TE properties of Bi_2Te_3 crystals and thin films have appeared. All this draws attention to studying the behavior of TE properties associated with the presence of a Dirac surface layer.

The report gives an overview of our studies of the TE properties of n- and p- Bi_2Te_3 and Bi_2Se_3 thin films with different thicknesses obtained by thermal evaporation in vacuum. We were the first to observe thickness oscillations of the kinetic coefficients in these thin films, and the character of their manifestation had a certain specificity as compared to conventional semiconductors [2-4]. One could expect that the Dirac cone structure of the surface states will influence the character of the thickness-dependent quantum oscillations. The significant amplitude of the oscillations and their practically undamped character allowed us to suggest that the observed peculiarities in the properties of these quantum size effects are connected with the specific properties of the surface layers inherent to TIs with the topologically protected surface states. The results obtained in these works represent an indirect confirmation of the specific properties of topological surface states and demonstrate the effect of the surface layers in TI thin films on quantum processes within the film volume. These results are important both for the development of the concepts of solid state physics and for practical applications of topological insulators jn thermoelectricity.

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THERMOELECTRIC AND THERMAL DIFFUSION PHENOMENA IN COLLOIDAL SOLUTIONS

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Thermoelectric and thermal diffusion phenomena in colloidal solutions Abstract: Interest in thermoelectric properties of colloidal solutions is currently due to a number of reasons. First of all, the systems are promising media for thermoelectrochemical generators - devices designed for the direct conversion of low-grade thermal energy of various industrial, transport, household installations into electrical energy. In addition, as recent studies show, thermoelectric phenomena have a significant effect on the transport of colloidal particles in an inhomogeneous temperature field, i.e. the study of thermoelectric phenomena in colloidal solutions and the regularities in them is also of fundamental interest.

Of particular interest is the study of the influence of the presence of inorganic ions in colloidal solutions on the value of thermoelectric EMF of colloidal solutions, which is investigated in this work.

In this work, experimental measurements of the thermoelectric EMF coefficient of pure colloidal solutions of technical tannin, starch and pine rosin and their mixtures with solutions of ionic electrolytes were carried out. Based on the experimental results, it can be concluded that the value of the thermoelectric emf of mixtures of colloidal solutions with ionic electrolytes depends on the ratio between the components of these mixtures.

With the predominance of the colloidal component in the mixture, the coefficient of its thermoelectromotive force tends to the value for a pure colloidal solution and vice versa. This work was supported by the Russian Foundation for Basic Research and Lipetsk regional administration (project no. 19-42-480001).

COMPUTER SIMULATION OF THE PROCESSES OF ZONE GROWING OF THERMOELECTRIC MATERIALS.

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Zone melting is one of the most commonly used methods for the production of semiconductor materials, in particular thermoelectric. However, obtaining thermoelectric materials (TEM) with the required properties is possible only under the conditions of a controlled crystallization process, since the curvature of the crystallization front, the temperature gradient at the interface between the solid and liquid phases, the geometry of the melt zone, and the velocity of zone motion have a great influence on the stability of growth and uniformity of a single crystal, etc [1, 2].

Computer simulation of TEM growing processes makes it possible to determine the growth conditions and explain possible difficulties that may arise as a result of changes in these conditions. It cannot replace, but presupposes and complements the experiment, providing information that can be experimentally obtained only indirectly. Therefore, the improvement and development of the technology for growing thermoelectric materials by means of multiparameter computer optimization of the controlled process parameters is urgent.

This paper presents an approach to constructing a computer model of the process of growing thermoelectric materials by the method of vertical zone melting. The developed model makes it possible to determine the optimal thermal conditions for growing single crystals based on Bi_2Te_3, to investigate the change in the shape of the crystallization front depending on changes in thermal conditions and growth rate, and also allows account for the Peltier effect occurring at the interface between solid and liquid phases of the grown material when electric current is passed through an ingot.

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INFLUENCE OF THERMOELECTRICITY ON CONVERSION EFFICIENCY OF SOLAR CELLS

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Efficiency of a single-junction solar cell is limited by the Shockley-Queisser theory which assumes that only photons having energy close to a semiconductor forbidden energy gap are used effectively. Photons of higher energy create electron and hole pairs, and the excess energy turns the photogenerated carriers into the hot carriers, with a nonequilibrium distribution temperature higher than the lattice. A solar cell loses about 30% of incident solar energy when the hot carriers thermalize, i.e., dissipate the excess energy to the lattice. Ross and Nozik proposed the idea of a hot carrier solar energy convertor in which the photogenerated hot carriers are extracted over a narrow range of energies at a rate faster than they dissipate energy to the lattice. Theoretically, the conversion efficiency of such a device can reach 66%. A large number of theoretical and experimental works devoted to the development of hot carrier solar cells werecarried out. However, no hot carrier solar cell valuable for practical applications is built yet. The hot carriers stipulate thermoelectromotive force formation across p-n junction. The polarity of thermoelectromotive force of hot carriers is opposite to that of classical photovoltage. Furthermore, thermalization of hot carriers leads to heating of the crystal lattice. The thermoelectromotive force caused by lattice heating also has polarity opposite to the classical´ one. Thus, carriers and lattice heating reduces the efficiency of a solar cell. In the presentation we demonstrate that photovoltage induced by a 1.06 micron laser pulse across GaAs p-n junction is composed of three components resulting from hot carrier and lattice heating, and electron-hole pair generation phenomena. The first one is very fast and shows polarity of thermoelectromotive force of hot carriers. The second one, resulting from thermalisation loss of hot carriers, has the same polarity and is slower. The third one, respectively, is the classical photovoltage arising due to two photon absorption with polarity opposite to that of the first two. Lattice heating and hot carriers thermoelectromotive force may be the reason of experimentally unattainable Shockley-Queisser limit

DEVELOPMENT OF THERMOELECTRIC ENHANCEMENT PRINCIPLES AND OUTLOOK FOR IOT ENERGY HARVESTING

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There is a vital need to develop technologies to dynamically harvest energy from surroundings to power IoT applications [1]. Thermoelectrics is promising, since it enables utilization of ubiquitous thermal energy like body heat. In regards to viable thermoelectric applications, the cost of materials appears not to be a critical factor (at the expense of material performance), but rather the appropriate processing and fabrication methods of effective modules. The thermoelectric performance remains a critical requirement, and in addition to various strategies for modules, such as utilizing semiconductor processes and novel hybrids [2], we have been trying to develop thermoelectric enhancement principles. As one such direction, we have tried to utilize magnetism, and have found that enhancement of the thermoelectric properties can be realized by magnetic interaction, via a) magnetic ion doping [3] and also embodied in magnetic semiconductors [4], and b) spin fluctuation [5]. The former has been demonstrated in magnetic transition metal chalcogenides like $CuFeS_2$, $CuCr_2S_4$, Cr_2Se, magnetic ion doped $CuGaTe_2$ and Bi_2Te_3, etc., while the latter has been embodied in Heusler alloys like Fe2VAl:Si. The magnetic semiconductor thermoelectric materials may also be compatible in the future with magnetic and spintronic sensors and devices. We have also utilized nanostructured materials with high ZT near room temperature such as the nanoporous rare earth free skuterudite with ZT~1@200^{o}C [6] and nano-oxide composite Bi0.5Sb1.5Te3 with ZT~1.5@70oC [7].

Recently, our collaborators have synthesized Heusler thin films with strikingly high ZT [8]. Defect and interfacial engineering has also yielded enhanced performance in GeTe, for example [9]. I will present an overview of these strategies and recent developments. References

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4. THERMOELECTRIC DEVICES AND EQUIPMENT

GENERALIZATION OF THE THEORY OF DESIGNING THERMOELECTRIC EQUIPMENT AND EXAMPLES OF ITS USE

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Thermoelectricity is rapidly expanding the areas of its practical use: from devices for the military, starting from reliable air conditioners to sensors for high-precision weapons; in medicine - for the diagnosis, prevention and treatment of many diseases; in space for cooling high-precision star-tracking devices and long-life generators of electrical energy; in industry - waste heat recovery devices; to household appliances - to ensure comfortable temperature conditions for a person's stay, storage of food products, and the like.

It is clear that such a variety of practical applications of thermoelectric equipment requires accurate and accessible methods for their design and optimization, this is especially important, realizing the constant competition from heat engines, compression refrigerators, etc.

However, activities aimed at improving the efficiency of thermoelectric equipment are primarily focused on the thermoelectric energy converters as such and reduce to increasing the figure of merit of thermoelectric materials for such converters. Nevertheless, it just as much depends on heat exchange devices. On the other hand, optimization of heat exchange systems without taking into account the ultimate purpose of their use does not give the desired result either.

In this work, an integrated approach to the design of thermoelectric equipment is used, based on the study of the most complete (generalized) physical models of thermoelectric devices, taking into account the presence of thermoelectric converters and systems that provide supply and removal of heat flows. Actual thermoelectric devices to provide the necessary heat exchange contain a whole system of heat exchangers (liquid, air, and combined), as well as heat exchange intensification devices - liquid pumps and air fans that consume electrical energy, while reducing overall efficiency. The power supply of such devices is also an optimization parameter, which is possible only in the case of complex optimization of the thermoelectric device.

The analytical solution of such problems of finding multiparametric optima is almost impossible, which leads to the necessity of applying computer optimization methods and design of such devices.

In general, the use of this approach makes it possible to increase the energy characteristics of thermoelectric devices by 10-20%.

Examples are provided of the use of these approaches for the design of specific thermoelectric devices - heat recuperators (thermoelectric generators for cement and steel furnaces, gas pumping units, automobile engines), heat pumps for a space-purpose water purification device, air conditioners (for vehicles, including military ones), individual air conditioners for humans, coolers for various radiation detectors, medical equipment, etc.

THERMAL DISTILLATION SYSTEM FOR DEEP SPACE MISSIONS

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New tests results of Centrifugal Multi Effect Distiller (CMED) with 3 and 5 stages with a thermoelectric heat pump are presented, the advantages of the design in comparison with analogues are shown. The best possibilities of using CMED for deep space missions are substantiated due to better efficiency, reliability, and good scalability of the system. The following paper provides new detailed information and data on the performance of the CMED. The possibility of achieving recovery up to 93%, good system scalability (performance from 1,5 to 7 litres per hour) and good quality of obtained distillate is shown.

THERMOELECTRIC COOLERS IN SPACE

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Thermoelectric coolers are widely used in space due to their undeniable advantages over other types of coolers. These benefits include:

1. Ability to work both in zero gravity and when exposed to overloads during maneuvers of spacecrafts in orbit, at launch and landing;
2. No need for a working substance (refrigerant or coolant);
3. The absence of moving parts resulting in the absence of acoustic noise, additional accelerations and vibrations;
4. Wide temperature range and easy control of operating modes.

The paper outlines specific applications of thermoelectric coolers:

- at space orbital stations for scientific experiments and the operation of crew life support systems;
- on orbital telecommunication and scientific spacecraft and interplanetary space stations for cooling and stabilizing the operating temperature of sensors of star trackers cameras, detectors of space telescopes.

The impossibility of replacing or repairing technical devices in spacecraft puts forward high requirements for the resource of thermoelectric coolers (reliability 120-150 FIT, life 18-20 years). The Institute of Thermoelectricity carries out the research aimed at ensuring the required reliability and durability of thermoelectric coolers. The paper considers the effect of degradation on the resource properties of thermoelectric materials, analyzes the current state and prospects of physical and computer models of degradation of thermoelectric materials and contact structures. Methods have been developed to significantly increase the reliability of thermoelectric coolers with series-parallel connection of legs, as well as passive redundancy of legs.

To increase the reliability of contact structures, a new type of connection has been developed, namely, bandage, which allows not only improving durability and resistance to high temperatures and ON / OFF cycles, but also increasing resistance to mechanical shocks. On the basis of the results obtained at the Institute of Thermoelectricity, designs and technology for the manufacture of highly reliable thermoelectric coolers for space purposes were developed. Specialized equipment has been developed and manufactured to test space coolers in vacuum in accordance with MIL-STD 883 and Telcordia GR-468 CORE.

SONE RELEVANT DIRECTIONS OF THERMOELECTRICITY APPLICATION IN MEDICINE

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The paper presents the results of research on the current state of application of thermoelectricity in various fields of medicine. Three main priority areas are identified - the use of thermoelectric cooling (heating) in medicine, the generation of electrical energy from human body heat and medical diagnosis using thermoelectric heat flux sensors.

Appropriate physical, mathematical and computer models of biological tissue have been built for these areas, taking into account thermophysical processes, blood circulation, heat exchange, metabolic processes and phase transition. Computer simulations have been made and the distributions of temperatures and heat fluxes in biological tissue in different operating modes have been determined. Based on the obtained results of computer simulation, thermoelectric medical equipment for the treatment and diagnosis of various diseases of the human body has been developed and manufactured.

The paper presents the design, principle of operation and technical characteristics of the developed thermoelectric medical devices. The results of clinical trials of such devices are presented. It is established that the results of the tests indicate the high prospects for the use of such thermoelectric medical equipment in medical practice.

THERMOELECTRIC POWER SUPPLIES IN EXTREME OPERATING CONDITIONS

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In technical means used in extreme conditions, in particular, in autonomous control systems at special facilities, the issue of being provided with appropriate sources of electricity is relevant. Such power supplies must have an optimal ratio of mass and size and energy characteristics, be resistant to shock loads up to 500^{-4}g, have a long (no less than 30-40 years) shelf life without maintenance, high reliability, etc.

A comparative analysis performed has shown that the most common chemical power sources (CFCs) of today are unable to solve such problem due to natural self-discharge, and, hence, short shelf life.

An alternative to providing power to disposable devices is the use of thermoelectric converters of thermal energy into electricity, the so-called thermoelectric generators with pyrotechnic heat sources, which the Institute of Thermoelectricity has extensive experience in since the 1980s.

This paper presents the results of research and development of a power supply of such type. It is established that classical thermocouple batteries are not always appropriate for solving the problems of this type, therefore, using the approaches of the generalized theory of thermoelectric energy conversion, special functional-gradient spiral thermocouples differing from thermocouples were created together with the technology of their fabrication with the account to requirements set for mass production.

Such sources meet the requirements of powering the destruction systems for precision weapons, impulse control systems in spacecrafts, providing automatic prevention of hazardous operating conditions at nuclear power plants and more.

METHODS OF OPTIMIZATION OF TEG PARAMETERS AND PROSPECTS OF THEIR APPLICATION AT THE ENERGY MARKET

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The presentation focuses on improving the efficiency of TEG by optimizing their parameters based on mathematical models that reflect the conditions of heat and electricity transfer in a system that includes a heat source, thermoelectric converter, cooling system and payload. The generalized results of previous researches which can benefit developers of thermoelectric generators are presented. Estimation of possible technical and economic indicators of TEG are given and the conditions under which this technology can ensure competitiveness at the energy market of today are formulated.

SOLAR PARABOLIC DISH COLLECTOR THERMOELECTRIC GENERATOR: EXPERIMENTAL STUDY

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Solar energy is one of the most important renewable energy resources. Electricity generation using photovoltaic panels by solar radiation is quite common. Thermoelectric generators are devices that convert solar thermal energy directly into electrical energy. Power is obtained in proportion to the square of the temperature difference between the surfaces. In this study, the thermal effect of the sun was increased by using a parabolic dish collector. TEG modules are sandwiched between copper heat sink and aluminium heat sink at the focal point at a distance of 60 cm. Tests were made in Tokat Gaziosmanpasa University in Turkey. While the hot surface temperature reached 181 degrees, the cold surface temperature was measured as 80 degrees. System efficiency was calculated as 3.1%. Power measured 5.1 W. It was concluded that TEGs can be used effectively in conjunction with concentrated solar energy.

THERMOELECTRIC VEHICLE LIQUID COOOLER

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The invention is a portable, compact, flexible, novel "Thermoelectric vehicle liquid cooler" with either circulation system or heat pipes. Within short period like a few minutes, it cools and heats water or water-like liquid by converting electrical energy from vehicle battery/electricity line into heat or cold without an intermediate material by using a flexible thermoelectric block composed of N and P type semiconductors.

In order to cool or heat a drink for one person within 5-10 minutes with the designed device, first 0.5 liter of water in a plastic bottle is put into the freezer part (cooler part) of the device and the device is powered either by battery or line voltage. By this, water or water-like liquid in a 0.5 liter plastic bottle in environmental temperature (35°C - 45°C) is cooled into 5°-10°C or heated into 30°C if it is cold with 3-5°C per per minute heating/cooling speed within 5-10 minutes, and the liquid becomes ready for service. The bottle shaped flexible thermoelectric block in the device cools or heats the liquid in the bottle directly and locally either with specially designed at least 2 solid based thermoelectric modules or with specially designed 42 flexible based flexible thermoelements. A vehicle battery or special SMPS power source is used to supply power to the thermoelectric vehicle liquid cooler. In order to minimize power consumption of the device minimum and to operate the device as a cooler or a heater, a special DC power and temperature control circuit is used. The device is made 'smart' by uploading a specially written software from computer to the control circuit. In order to keep the temperature of the heating side of the flexible thermoelectric block at the environmental temperature, a heat transfer system with a closed circulating water-cooling with radiator-fan or aluminum-fan or specially designed heat pipes is used.

IMPEDANCE SPECTROSCOPY FOR THE ASSESSMENT OF THERMOELECTRIC MODULES AND GENERATORS

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In this work, we present recent new developments of the impedance spectroscopy method applied to (i) thermoelectric devices operating under actual energy generation conditions (small temperature difference), and (ii) the assessment of thermal contact resistances inside the thermoelectric devices (mainly at the thermoelement/metallic electrode junction) by measuring the module suspended. The studies show for the first case that the thermal contact resistance between the thermoelectric module and heat source/sink plays a crucial role in the impedance response [1]. In fact, we show how the impedance spectroscopy technique can be used to quantify these thermal contacts. For the second case, we present a new theoretical model which covers the thermal contact resistance between the thermoelectric legs and the metallic electrodes, the influence of these metallic strips, the thermal contact resistance between the metallic strips and the ceramic layers, and a new spreading-constriction impedance element that extends the usability of the method [2]. This new equivalent circuit can be used to assess thermoelectric modules and opens up the possibility of using the impedance method as a control quality tool to detect weaknesses in thermoelectric modules.

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5. POSTERS

METHOD FOR CONTACTLESS DETERMINATION OF THE EFFICIENCY OF ANISOTROPIC THERMOELECTRIC MATERIALS

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The possibilities of modern methods for determining the efficiency of thermoelectric materials, as well as reducing the errors of its measurement, are mainly determined by the electrical contacts used [1, 2].

The peculiarities of thermoelectric phenomena in anisotropic media make it possible to solve this issue by the eddy-current contactless method [3].

This method is based on direct contactless determination of the values of the longitudinal and transverse components of the tensors of adiabatic and isothermal values $\sigma_{\parallel}^{\alpha}, \sigma_{\perp}^{\alpha}$ *and* $\sigma_{\parallel}^{u}, \sigma_{\perp}^{u}$ of electric conductivities, later on used to calculate the values of the efficiencies Z_{11} and Z_{22} in the required crystallographic directions. Wherein:

$$Z_{11} = \left(1 - \frac{\sigma_{11}^{i} - \sigma_{22}^{i}}{\sigma_{11}^{\alpha} + \sigma_{22}^{\alpha}}\right) \cdot T^{-1}; \quad Z_{22} = \left(1 - \frac{\sigma_{11}^{i} - \sigma_{22}^{i}}{\sigma_{11}^{\alpha} - \sigma_{22}^{\alpha}}\right) \cdot T^{-1}$$

The proposed method makes it possible to automate the process of measuring parameters and control thermoelectric ingots, billets and parts, as well as selects p - n pairs.

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ON THE ELECTRONIC, OPTICAL AND THERMOELECTRIC PROPERTIES OF CORDEROITE-TYPE NANOMATERIALS

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The remarkable progress was achieved in the study of the physical and chemical properties of Hg3X2Y2 (X= S, Se, Te; Y= F, Cl, Br, I) crystals. Their electronic and optical properties such as high refractive index, photoconductivity, electrooptical effect, optical activity, optical nonlinearity etc., make them promising nanomaterials for nonlinear application. The electronic, optical and thermoelectric properties depend sufficiently on synthesis conditions, structural defects, and morphological characteristics. From the structural point of view, the crystals under investigation are well ordered, and observed that the basic structural unit in the title crystal is a

[XHg3] pyramid. The structure consists of two sets of octahedral spirals with different radii and twisting directions. These crystals possess an excellent transparency in the mid-IR spectral range. Due to these features, the corderoite-type crystals in nanoparticle form have a wide range of applications in nanophysics.

Obtained data suggest that the physical properties of the Hg3X2Y2 crystals should be taken into account in the studies concerning the improvement of the thermoelectric devices. At the same time due to the transparency of corderoite family compounds in the wide region of the visible and IR-range (from 0.3 to 40 mcm) creates new opportunities for materials design. They have a great potential for wide range of possible applications in: thermoelectric devices, energy converters (modules), elements for dynamic holography, recording and information storage, modulators, deflectors and other devices based on the phenomenon of the interaction of light beams.

ELECTRO-OPTIC EFFECT IN THE $Hg_3Se_2F_2$

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$Hg_3Se_2F_2$ crystal is of high interest for both researchers and engineers due to the physical properties and great potential for development of electronic, thermoelectric and optoelectronic devices. The main structural feature of the mercury chalcogenide-halogenides is the tendency to formation of various polymorphic modifications due to the great conformational capacity of mercury-chalcogen component. Nanomaterials based on them are expected to contribute in the development of nanophysics.

This paper presents the electro-optic effect in the Hg3Se2F2 crystal. To understand better the second-order polarization induced in the crystal and occurrence of the electro-optic effect the detailed theoretical analysis is conducted. The space-charge field changes the refractive index due to the electro-optic effect. The electro-optic tensor for Hg3Se2F2 crystal is calculated. Symmetry considerations permit simplification of the general view for this tensor. The nonzero coefficients of 3th rank electro-optic tensor are r41= r52= r63. These data give fundamental information and experiences for further studies.

STRUCTURE AND THERMOELECTRIC CHARACTERISTICS OF THIN FILMS BASED ON LEAD TELLURIDE

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The results of the investigations of structural and thermoelectric properties of thin composite films based on PbTe are given. The films of different thicknesses (10–150 nm) on glass, Al_2O_3 and silicon substrates were obtained by pulsed laser deposition of 1 × 10−4 Pa, and at different substrate temperatures (30 ^oC, 200 ^oC). The growth conditions leading to the films having different properties that could be controlled in a possibly wide range were identified. The parameters of the crystalline structure of thin films have been determined by X-ray diffractometry methods and high-energy electron diffraction methods. The surface morphology of thin PbTe composite films (initial growth stages) was investigated using a SEM scanning microscope. During the study of the morphology of the film surface, it was clearly visible that the contrasts with the main surface (matrix) of the film differ. This indicates a rather significant deviation from the stoichiometry in the process of the deposition of the films by the method of pulsed laser deposition.

The temperature dependences of electrical conductivity, the Seebeck coefficient and the thermal power of thin composite films based on PbTe with inclusions have been investigated. With increasing temperature, Zeebek coefficient for the PbTe film Sb_2Te_3 increases in absolute value from 1mV/K to values 11mV/K, and the electrical conductivity decreases from 0.5 $(Ohm \cdot cm^{-1})$ to 0.08 $(Ohm \cdot cm^{-1})$. For other films, the temperature characteristics of the similar parameters have the opposite character. The estimation of the value of thermoelectric parameters is made taking into account the dimensional effects in the processes of charge carrier transport, and the phenomenon of increase of the Seebeck coefficient at the content of Bi_2Te_3 is indicated.

THERMOELECTRIC COOLERS OF X-RAY RADIATION DETECTORS

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X-ray methods are widely used for non-destructive microanalytical studies of the structure and composition of materials with high spatial resolution. The current state of the art of nuclear microanalysis methods using focused ion beams of MeV energies with high monoenergeticity (ΔE / E = 10-5) makes it possible to achieve spatial resolution over the surface of up to 100 nanometers and up to 10 nanometers over the thickness of samples. A further increase in resolution substantially depends on the improvement of the analytical characteristics of semiconductor detectors, as well as on the use of new types of wide-aperture position-sensitive radiation detectors.

To increase the resolution of X-ray detectors, it is important to solve the problem of ensuring the optimum temperature of their operation. It is solved by using semiconductor thermoelectric cooling modules, which provide the required cooling depth in the minimum working volume of the detector. Thus, single-stage thermoelectric modules are used for shallow cooling (up to 250 K), two-stage TECs are used to cool sensors to an operating temperature of 230 K, three-stage TECs are used to a temperature of 210 K, four and five-stage TECs are used to temperatures below 190 K.

The aim of the work is to analyze the possibilities of thermoelectricity for cooling X-ray detectors, and to develop a design for a multistage thermoelectric cooler for X-ray detectors.

Using computer approaches, the design and characteristics of a thermoelectric cooler as part of an X-ray detector are calculated. TE cooling module contains 4 cascades of thermoelectric material based on Bi_2Te_3 with overall dimensions - 12 x 16 x 12 mm, providing the area of the cooled pad 4 x 8 mm. The electrical power of the thermoelectric converter was determined to be W = 2.85 W, which, with a coefficient of performance ε = 0.02, provides the detector base temperature T = -70 ° C and the temperature difference ΔT = 90 K.

INFLUENCE OF SUPERLATTICE-BASED HETEROCONTACTS DESCRIBED BY THE FIVAZ MODEL, ON THE WORK OF THERMOCOUPLE THERMOELEMENT IN COOLING MODE

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In this paper, the temperature dependences of the electrical resistance of superlattice-based bismuth telluride-nickel heterocontacts described by the Fivaz model are calculated. In so doing, diffusion of nickel into thermoelectric material was assumed to be unsteady. The calculations were carried out both with and without account of percolation effect related to formation of clusters. It is shown that at high degrees of openness of the Fermi surface of thermoelectric material in the near-contact area, hence, the nonparabolicity of its band spectrum described by the Fivaz model, the electrical contact resistance of thermoelectric material-metal transient layer in the temperature range from 200 to 400 K and transient layer thickness from 20 to 150 μm weakly depends on the peculiarities of distribution of nickel atoms or clusters in thermoelectric material and varies within $8\cdot10^{-9}$ to $4.5\cdot10^{-7}$ Ohm·cm^2. This phenomenon takes place because the resistivity of thermoelectric material with a band spectrum described by the Fivaz model at a high degree of openness of the Fermi surface, and, hence, the nonparabolicity of the band spectrum of thermoelectric material in the near-contact area drastically decreases and approaches the resistivity of metal. This makes it possible, in contrast to traditional contact structures, to reach almost the limiting values of the cooler output parameters in the temperature range from 225 to 300 K. In this case, the limiting value of temperature difference reaches 74 K, and at the difference of 65 K the cooling capacity is 0.5 W. Note also that in the case of heterocontacts the difference of 72 K is reached at a current of 5 A, and in the case of traditional contacts – the difference close to 70 K at a current of 6 A.

GYROTROPIC THERMOELEMENT IN A HOMOGENEOUS AND INHOMOGENEOUS MAGNETIC FIELDS

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One of the most promising trends in the progress of thermoelectricity is the development of new types of thermoelements, including gyrotropic ones, and a more detailed study of traditional thermoelements. In recent years, a number of works on gyrotropic thermoelements in constant magnetic fields [1-3] have been published; their parameters in inhomogeneous magnetic fields have also been considered [4]. These possibilities are used but little, therefore their development will allow increasing the element base of thermoelectricity, improving the

competitive ability of thermoelectric converters and gyrotropic thermoelements, and developing more advanced thermoelectric products based on them, with improved quality and reliability.

To study the parameters of gyrotropic thermoelements, it is necessary to solve the following equation of thermal conductivity with the corresponding boundary conditions:

$$\kappa\Delta T + \rho_0 j^2 + 2\alpha_\perp \left(j_y \frac{\partial T}{\partial x} - j_x \frac{\partial T}{\partial y} \right) = 0,$$

where T is the temperature, κ is the coefficient of thermal conductivity of a gyrotropic medium; ρ_0 is the specific electrical resistance; x, y are coordinates; j, j_x, j_y are module and projections of the electric current density vector; $\alpha_\perp = Q^\perp B$ is an asymmetric part of thermoEMF tensor; $Q^\perp$ is Nernst-Ettingshausen coefficient; B –is the magnetic field induction.

Using computer simulation, the temperature distributions in the working medium of gyrotropic thermoelements of rectangular, spiral and optimal shapes for various thermoelectric materials in a uniform and non-uniform magnetic field have been determined. The temperature dependences of the efficiency of gyrotropic thermoelements in a uniform and non-uniform magnetic field are determined. It has been established that the efficiency of generator gyrotropic thermoelements is higher in a non-uniform magnetic field than that in a uniform field. A deeper cooling was also obtained for the case of an non-uniform magnetic field.

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Z-METERING OF SINGLE THERMOELEMENTS

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The Z-metering method is widely used both in the production of thermoelectric modules and in experimental studies. Basically, this is an express control of the parameters of the finished thermoelectric modules: generators; coolers. It allows characterizing the cooling performance, and some other parameters. However, in practical production and in experiment, it is important to predict at the initial stages these output parameters of the products based on the properties of the thermoelectric material defining them. Methods for controlling the parameters of initial thermoelectric materials are not enough for this. Such testing is usually limited to determining the electrical conductivity and Seebeck coefficient of the material, which is not enough.

This paper presents the results of the development of the Z-metering method of a single thermoelements.

Theoretical calculations and experimental studies have shown that on unit thermoelements of a practical nomenclature (working sizes for thermoelectric modules), quality parameters can be measured with high accuracy, and, therefore, the assumed parameters of thermoelectric modules from these thermoelements. The results of the experiments well confirm the calculation data. Such Z-meterings, subject to methodological recommendations, produce results that very reliably reflect the expected parameters of the finished modules. The method can be recommended for practical application.

METHODS AND EQUIPMENT FOR PRECISE DETERMINATION OF PARAMETERS OF THERMOELECTRIC GENERATOR MODULES

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Improving the quality of thermoelectric generator modules, reducing their cost requires the use of advanced technological methods and highly efficient materials in their development and manufacture. Improving the accuracy in determining the thermal and electrical parameters of modules makes it possible to more predictably adjust the technology of manufacturing modules, as well as to optimally approach the direct creation of final devices based on generator modules.

Analysis of literary sources, publications and messages in electronic media makes it possible to conclude that little has been done in the direction of metrology of generator modules and means of control of their quality, or such information is closed and inaccessible to non-corporate specialists. The existing installations and stands are rather sophisticated and are more scientific than applied. They permit, of course, to determine the parameters of the modules, but it is ineffective to use them even for small-scale production of generator modules.

The paper describes the design of an installation for measuring the properties of thermoelectric generator modules. The method of calibration of a heat meter and the results of estimation of its errors at definition of efficiency of generator modules are presented.

The installation developed at the Institute of Thermoelectricity is universal - with a wide range of standard sizes of modules that can be measured, a wide temperature range and a power range of modules on a controlled load. Installation is easy to use, inexpensive, allows one to transfer measurement results to a computer and process them using non-specialized software, which makes it attractive and accessible to a wide range of users who deal with thermoelectric generator modules.

Based on the analysis of heat flows, the accuracy and main errors in determining the parameters of the generator modules were estimated. The properties of a thermoelectric generator module can be measured in a time not more than 30 minutes, with an accuracy of 1% for electrical parameters and up to 5% for thermal parameters

THERMOELECTRIC AIR CONDITIONING IN THE BEEHIVES

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Global warming, the spread of diseases in bees, the need to increase the profitability of apiaries, on the one hand, and the development of solar energy, thermoelectric devices, computer technologies, on the other one, create the basis for building new hives with the possibilities of optimal annual beekeeping. It has been proven by practice that bee colonies in summer, housed in shaded areas, swarm less, develop better and collect more nectar than bee colonies in open areas. It follows from this that the issue of air conditioning in the hive is an actual task for beekeeping.

Usually, under natural conditions, the bee colony regulates the temperature and humidity of the air in the hive with the help of:

a) forced ventilation by the bees of the hive;

b) creeping out from the hive part of the bees;

c) a decrease in the number of bees on the combs.

Under these circumstances, the development of families is inhibited and the collection of nectar is reduced.

This paper discusses the prospects for using the latest technologies to create modern thermoelectric hives with the possibility of year-round regulation of temperature and humidity. The use of thermoelectric modules in combination with fans allows you to change the temperature regime of the hive in the desired direction: either to heat or cool it.

Unlike resistor heaters, thermoelectric modules have a double function. These are solid state devices that convert electrical energy into a temperature gradient known as the Peltier effect. They are quiet, reliable and durable. With the help of a fan, cooled or heated air can be forced to a certain distance inside the hive, which is necessary to change the microclimate in the hive. For autonomous power supply of the modules, the use of solar panels in combination with a battery is assumed.

An important aspect of using thermoelectric modules is their environmental friendliness in the fight against varroatosis and other diseases of bees. For example, by briefly raising the temperature in the hive, you can effectively control the Varroa Jacobsoni mite.

EXPERIMENTAL STUDIES OF THE COOLING RATE OF THERMOELECTRIC INDIVIDUAL AIR CONDITIONER FOR HUMANS

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The paper analyzes the available scientific and technical information on the state of affairs in the use of individual air conditioners for humans. The possibilities of their wide practical use to ensure comfortable conditions for a person's stay in various temperature conditions and with a change in body heat transfer depending on the mechanical loads of the body (running, hard work) and the type of activity (sports, military, medical, etc.) are shown. Unlike the traditional approach to conditioning of the entire air in a room where a person is located, its local conditioning can reduce energy costs by tens and hundreds of times. Moreover, such air conditioners are compact, quiet and reliable in use.

The above indicates the relevance of research aimed at developing individual air conditioners for humans, which, by and large, can affect the conditions and lifestyle of mankind, which will be due to the transition from "passive" clothing, which still serves mainly as a thermal insulation of human organism, to the use of "active" clothing, which responds to changes in temperature conditions of human activity.

The paper analyzes and classifies physical models of individual air conditioners for humans and identifies their most rational options that require further research and optimization, taking into account the specific conditions of their operation.

THERMOELECTRIC PRE-STARTING HEATERS FOR VEHICLES

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To overcome the difficulties associated with the operation of vehicles at low temperatures, various means of thermal pre-starting of internal combustion engines (ICE) start being used widely. The most effective among such means are pre-starting heaters, which are flame heat sources that operate on fuel from vehicles and heat the engine coolant. In addition to the reliable start of the internal combustion engine, the use of prestart heaters creates conditions for saving on average about 90 to150 liters of fuel per season, reduces the toxicity of exhaust gases up to fivefold during engine warming up and allows increasing the engine life by 200 to 300 km per start when warming up from temperature (-20 ÷ -30) ° C.

The determining factor to limit the possibility of mass application of pre-starting heaters is the discharge of the battery during the operation of the pre-starting equipment.

One of the promising methods for solving the problem of discharging batteries during thermal preparation of vehicle engines for start-up is the use of thermoelectric generators as sources of electrical energy for pre-start heaters. This idea is the basis of the research carried out at the Institute of Thermoelectricity, and aimed at creating thermoelectric pre-starting heat sources for passenger car engines. As a result of the research carried out, an experimental model of a thermoelectric pre-heater on diesel fuel with a thermal power of 3 kW was developed for preheating internal combustion engines with a volume of up to 4 liters. The heater contains a thermoelectric generator with an electric power of 80 to 100 W, which operates from the heat of the starting heater and provides power to its components.

To use such sources of heat and electricity for improving the operational capabilities of high-power equipment, the electric power of the thermoelectric generator should be about 300 to 500 W. Such thermoelectric devices must have a long service life, be reliable and resistant to mechanical stresses.

The analysis of optional physical models of the "thermoelectric generator – pre-starting heater" system showed that the most attractive in terms of efficiency and ease of handling is the system in which the pre-starting heater and generator are combined by one hydraulic circuit. Such a heater can be installed separately, in an accessible place in the vehicle, which makes it easier to implement.

A thermoelectric generator in such a system works as follows. The thermal energy obtained as a result of fuel combustion heats up a hot heat exchanger, passes through a thermoelectric battery and is removed through liquid heat exchangers, in which the coolant circulates, to a hydraulic circuit common with the pre-heater. Due to the temperature difference between the hot and cold sides of the thermopile, an electric current is generated, which is used to power the pre-heater, as well as all the electrical elements of the generator itself.

The evaluation of the energy characteristics of thermoelectric generators for autonomous preheating systems for high-power equipment when using serial heaters with a thermal power over 15 kW is carried out. It has been established that the efficiency of the "thermoelectric generator – pre-starting heater" system for most heaters is at the level of 75-80%. At the same time, taking into account the thermal power generated by the thermoelectric generator, more powerful modifications of the heaters can be replaced by an autonomous system, which consists of a less powerful heater and a thermoelectric generator, which provides the entire system with electrical energy.

TERNARY SYSTEMS OF CADMIUM AND ZINC ANTIMONIDES

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An integrated approach has been developed for calculating the parameters of the electronic structure of hybrid orbitals of nonequivalent chemical bonds. The results of theoretical calculations of the concentration dependences of interatomic distances in the crystal structures of $Zn_xCd_{1-x}Sb$ are presented, and the features of the thermodynamic functions were investigated by constructing isothermal sections of ternary systems of antimonides of different compositions: In-Cd-Sb, In-Zn-Sb, Ga-Cd-Sb, Ga- Zn-Sb, In-Ga-Sb. Calculations of effective charges, effective radii and dissociation energy of the respective chemical bonds are carried out. The results obtained agree with the calculations of chemical bond parameters by the methods of microscopic theory, with the results of studies on thermal rearrangement of atoms in the melts and can be used in the development of technological modes for the synthesis of new materials based on $Zn_xCd_{1-x}Sb$.

HEAT CAPACITY OF $Bi_2(Te_{1-x}Se_x)_3$ SOLID SOLUTIONS

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Solid solutions (SS) of $Bi_2(Te_{1-x}Se_x)_3$ system are widely used for thermoelectric (TE) cooling in devices that operate near room temperature [1]. Bi_2Te_3 and Bi_2Se_3 crystallize in a rhombohedral lattice and form a series of continuous SS. In our previous works [2] we observed concentration anomalies of mechanical and TE properties in this system near $x \sim 0.01$, that were related to the implementation of phase transition of percolation type from the diluted to concentrated SS. Determining the type of dependence of the heat capacity C_p of temperature (or, as in this case, the composition of SS) can be considered a direct method of detecting second-order phase transition. In this connection, to clarify the nature of the anomalies of properties in $Bi_2(Te_{1-x}Se_x)_3$ solid solution, it is interesting to study the dependence of C_p on composition in the region of low impurity content.

The purpose of this work was to study the dependence of C_p on the composition of $Bi_2(Te_{1-x}Se_x)_3$ SS in the range of ($0 < x < 0.06$) at room temperature. Samples for the study of C_p were cold-pressed tablets that were made of cast polycrystals $Bi_2(Te_{1-x}Se_x)_3$ by grinding, pressing the powder under a pressure of $P = 7$ t/cm^2 for 1 minute and subsequent annealing at $T = 575$ K for 200 hours. Heat capacity was measured by the dynamic calorimeter method on the installation IT-*C*-400 in the temperature range of $T = 150 – 625$ K.

It is shown that the concentration dependences of C_p are of non-monotonic nature, just as the concentration dependences of TE properties [2]. In the range of compositions $x = 0.0075$ - 0.025 an anomalous peak of C_p with a maximum C_p at $x = 0.02$ was detected, the existence of which is related to the implementation of percolation type phase transition from diluted to concentrated SS. The observed peak can be interpreted as a λ-peak, similar to that accompanying second-order phase transition. The research results further confirm the assumption about the critical nature of changing the properties in $Bi_2(Te_{1-x}Se_x)_3$ SS with a low impurity content.

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THERMOELECTRIC CONVERTERS OF ALTERNATING CURRENT

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Under AC TE converter we understand a device based on the principle of converting electrical energy of measured values into thermal energy, which is released in a resistive heater, with its subsequent transformation into thermoelectric power of a thermocouple [1].

The paper shows that scientific research and AC TE converters have been a traditional direction of research at the Institute of Thermoelectricity since the 70s of the last century. The use in these developments of highly efficient thermoelectric materials optimized for thermoelectric converters opened up prospects for the development of a new generation of measuring equipment, the characteristics of which outperform the known analogs. For clarity, the paper contains information on the comparative parameters and characteristics of TE converters created at the Institute.

Based on the theory of semiconductor TE converters created at the Institute of Thermoelectricity, a number of AC tools for AC measuring equipment were developed and introduced into production, namely digital voltmeters, ammeters, wattmeters, devices for measuring electromagnetic field energy, current pulses, etc. However, this does not exhaust the possibilities of practical application of TE converters. Research and development of TE converters for measuring equipment using semiconductor thermocouples is just beginning, which confirms the priority of the Institute of Thermoelectricity in this area.

Widespread introduction of energy-saving technologies in all sectors of the economy requires increasingly high-quality control of AC energy values of different frequency and waveform. Despite the rapid development of measuring instruments based on other principles, devices based on thermal converters occupy a prominent place, and leading metrological centers in different countries are working to develop and improve thermal converters for state standards and reference measuring instruments for current, voltage, power and power factor. A dramatic proof of the possibility of practical application of TE converters was the creation of a TE converter for the military secondary standard VVTU 48-07-01-09 of the electrical voltage unit in the frequency range from 10 Hz to 30 MHz. Such a standard, according to the order of the Minister of Defense of Ukraine dated October 18, 2010, No. 529, was adopted to provide the Armed Forces of Ukraine with new modern technical means to ensure the uniformity and accuracy of measurements.

Absence in Ukraine of the primary state standard of electric voltage in the frequency range in 1 MHz to 30 MHz necessitates the use of standards of other countries (Russia) for metrological maintenance of electric voltage unit in this frequency range. A significant part of the military equipment of the Armed Forces of Ukraine operates in the specified frequency range and the lack of a primary standard negatively affects the quality of such equipment. Currently, the Institute has created a high-precision AC TE converter for the primary state standard of AC voltage in the radio frequency range.

The possibilities of practical applications are not limited to the above-mentioned directions as confirmed by the lists of the priority areas of using TE converters and their potential consumers given in the work.

EFFECT OF DEVIATION FROM STOICHIOMETRY ON THERMAL CONDUCTIVITY OF BI_2SE_3 POLYCRYSTALS

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Bi_2Se_3 is the well known *n*-type thermoelectric (TE) material for cooling devices. It belongs to a narrow-gap semiconductor group and demonstrates the unique properties of topological insulator (materials which are dielectric in bulk with a conducting layer on the surface). The efficiency of a TE convertor depends on the value of TE figure of merit Z ($Z = S^2 \cdot \sigma / \lambda$, where σ and λ are the electrical and total thermal conductivities, respectively, S is the Seebeck coefficient of a TE material). It is known, that the deviation from stoichiometry in chemical compound leads to the variation in concentration of intrinsic defects which largely determine the properties of material. Therefore it is important to study the effect of deviation from stoichiometry on the properties of Bi_2Se_3 crystals. As far as we know, no studies of the thermal properties of Bi_2Se_3 polycrystals under the deviation from stoichiometry have been conducted yet.

The goal of the work is to study the effect of deviation from stoichiometry on the thermal conductivity of Bi_2Se_3 polycrystals.

The samples were synthesized by fusing high purity Bi and Se in evacuated quartz ampoules at 980 K and subsequent annealing at 820 K for 200 hours and cooling to room temperature in the turned off furnace. In this way were obtained Bi_2Se_3 polycrystals with the concentrations varied in the range (59.9 - 60.0) at. % Se. The pressed samples were obtained by cold-pressed method (a load of 400 MPa for 60 s) with subsequent annealing in evacuated quartz ampoules at 670 K for 250 h. The thermal conductivity λ was measured by the dynamic λ-calorimeter method in monotonic heating regime with help of IT-λ-400 experimental facility. The errors of λ measurement did not exceed 5%.

It was established that the dependence of λ of Bi_2Se_3 polycrystals under the deviation from stoichiometry to the Bi-rich side exhibit the non-monotonic behavior. The observed result is attributed to a change in the defect structure and phase composition under the deviation from stoichiometry.

THERMAL CONDUCTIVITY OF $Pb_{1-x}Sn_xTe$ SOLID SOLUTIONS IN THE FIELD OF ZONE INVERSION

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Narrowband semiconductor solid solutions (TP) Pb1-xSnxTe are well known as materials used in the production of p-legs of thermoelectric converters [1]. A feature of the structure of Pb1-xSnxTe SS energy zones is the inversion of zones and the realization of a gapless state at certain values of *x*, which leads to the appearance of a topological nontrivial phase protected by the spatial mirror symmetry of the crystal [2]. Earlier, we observed extremes on the dependences of microhardness and heat capacity on the composition in the range x = 0.59 - 0.68 at room temperature at x □ 0.62, the presence of which we attributed to the transition to a gapless state [3]. Therefore, it was of interest to find out whether the effect found in [3] will manifest itself on thermal conductivity (λ).

Pb1-xSnxTe polycrystals (x = 0.59 - 0.68) were obtained by direct fusion of the initial components in evacuated quartz ampoules. Samples for measuring λ were made by hot pressing of powders. Thermal conductivity was measured in the temperature range of 150-600 K using the device IT-λ-400 by the dynamic calorimeter method in the mode of monotonic heating. The scatter of the obtained values of λ for each sample did not exceed 5%.

As a result of the measurements of λ, it was shown that, with a general tendency to an increase in λ with an increase in the Sn content, a peak is observed in the λ (x) dependence in the composition range x = 0.6125 - 0.6275. Thus, zone inversion and the realization of a gapless state in $Pb_{1-x}Sn_xTe$ is manifested due to the appearance of extremes in the properties, caused by changes not only in the electronic, but also in the phonon spectra.

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THERMOELECTRIC AIR-CONDITIONERS FOR ARMORED VEHICLES

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In modern armored vehicles, in particular tanks, of the leading countries of the world, air conditioning is actively used to ensure the working conditions for the crew. The use of such air conditioners at elevated ambient temperatures is especially relevant. Analysis of literary sources indicates that staying of people in conditions of high ambient temperatures for a long time significantly reduces the efficiency of their work, and with a significant rise in temperature, there is also a risk of loss of consciousness. This jeopardizes the ability to fulfill the assigned combat missions. On the other hand, with a sharp drop in air temperature inside the tank, there is a risk of acute respiratory diseases, which also reduces the efficiency of the tank crew.

The literature provides data on air conditioning in vehicles, in particular armored vehicles, by various methods. Particular attention is paid to the use of compression air conditioners. This is due to their relatively high efficiency. However, they also have a number of disadvantages, in particular, the presence of environmentally hazardous refrigerants, low reliability, sensitivity to mechanical overload and orientation in space, which significantly reduces the attractiveness of using compression air conditioners. This situation is especially relevant when using these air conditioners in military equipment, which is due to the presence of increased requirements for their reliability. These disadvantages are eliminated by using thermoelectric air conditioners (TEC).

Analysis of the literature testifies that TE air conditioners have gained the widest acceptance in Russian Federation. All serial models of Russian tanks (including export models), starting from T-90M “Breakthrough-3” (in service since 2018), are equipped with TE air conditioners produced by AO “Scientific and Production Corporation “Uralvagonzavod”. Besides, ZAO "Air Conditioner" carries our serial production of TE air conditioners for tanks T-14 “Armata”.

Active research into the conditioning of tanks in high temperature conditions is underway in India. The TE air conditioner was integrated into the main Indian battle tank Arjun (in service since 2006) and was successfully demonstrated at the Main Research Laboratory in Avadi (CVRDE) and at the Mahajansky field shooting range in Rajasthan (Indo-Pakistani border) in June 2005.

The development of TEC for military equipment (including tanks) is also carried out in companies of the leading countries of the world, in particular EIC Solutions Inc. (USA), TECA Corporation (USA), Marlow Industries, Inc. (USA), Global Thermoelectric, Inc. (Canada).

This paper presents the results of calculations of the limiting capabilities of the TE air conditioners for armored vehicles using real requirements for their operation. Comparison of the results obtained with the parameters of known TE air conditioners for tanks indicates the possibility of their improvement in energy efficiency by ~ 30%, which opens up opportunities for further improvements in such air conditioners.

THERMOELECTRIC HEAT PUMPS FOR SPECIAL APPLICATIONS

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The results of research and development of thermoelectric heat pumps intended for special use are presented. Thermoelectric devices have important qualities for this purpose: high accuracy of temperature control, no danger of contamination by liquid refrigerant vapors, high resistance to mechanical stress, low weight and volume, virtually no acoustic noise, and a long service life.

Computer simulation methods have been used to determine optimal parameters of thermoelectric modules, heat exchange systems for supply and removal of heat from a heat pump in a given operating temperature range, modes of electrical power supply of modules; the efficiency of the structural division of the heat pump into sections operating in a specific temperature range to achieve maximum efficiency of the heat pump has been shown. When developing the design of the heat pump, special attention was paid to reducing its weight and size characteristics. The paper presents the results of a study of thermoelectric heat pumps developed for defense technology: submarines, Kolchuga-type radar stations, as well as for use in space flight.

For sectional thermoelectric heat pumps, single-stage modules have been developed from Bi_2Te_3 based materials, optimized for the hot side temperature level of 50-100 ° C. It is shown that when single-stage modules are used in the sections of the optimal power supply mode, the efficiency of a sectional heat pump is 1.2 times that of the heat pumps created according to the traditional single-section scheme.

Designs of heat pumps of various special applications are described, the results of research on their parameters and characteristics are given.

CLASSIC DIMENSIONAL EFFECT IN $Bi_2(Te_{0.9}Se_{0.1})_3$

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Solid solutions$(Bi_{1-x}Se_x)_2Te_3$ are well known as the best materials for n–type legs of thermocouples operating at temperatures of 300 to 450 K [1]. The growing interest in the study of nanostructures in thermoelectricity and the increasing use of thin-film thermocouples are drawing attention to the study of these materials in the 2D state. This, in its turn, stimulates the study of dimensional effects, the presence of which leads to the modification of properties, resulting in the size of the system becoming a parameter that allows control over its properties.

The objective of the work is to study the classical dimensional effect in thin films of $Bi_2(Te_{0.9}Se_{0.1})_3$ solid solution by measuring the Seebeck coefficient. The objects of research are thin films with thicknesses d ~ 16 - 178 nm, grown by thermal evaporation in vacuum of $Bi_2(Te_{0.9}Se_{0.1})_3$ polycrystal with subsequent condensation on glass substrates. Measurement of the Seebeck coefficient S at room temperature for films and polycrystals was performed by the differential method at a temperature gradient $\Delta T = 2$ K.

It was established that in films obtained from the p-$Bi_2(Te_{0.9}Se_{0.1})_3$ crystal, the type of conductivity changes from hole one to electronic one. This "donor" effect, which is also observed in pressed massive crystals [2], can be explained by the stresses arising in the film during cultivation and (or) changes in equilibrium conditions during the transition from crystal to film due to the fact that a significant contribution to the film free energy begins to introduce surface energy.

When the film thickness increases from 16 to 110 nm, an increase in S is observed almost fourfold, after which the dependence *S (d)* reaches saturation, i.e., a classical dimensional effect occurs. Using the Mayer equation allows obtaining a good agreement between the results of theoretical calculation and experimental data and calculating the value of the average free path length of electrons and the mirror parameter.

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HOUSEHOLD THERMOELECTRIC REFRIGERATOR IN QUASI-STATIONARY MODE

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The paper considers a theoretical method for assessing the energy efficiency of a thermoelectric refrigerator in a quasi-stationary mode. A physical model of a thermoelectric refrigerator in a quasi-stationary mode has been developed and its mathematical description has been performed. The main approximations that are allowed when using the model have been posed.

Evaluations of the amount of energy consumption of a thermoelectric refrigerator with a chamber volume of 67 liters to achieve an operating temperature in the chamber of 5 ° C have been performed. It is shown that the use of a quasi-stationary cooling mode is justified for the operation of thermoelectric household refrigerators due to their high heat capacity. The result was obtained that when using a quasi-stationary mode, power consumption is reduced by about 17% compared to using a DC mode to achieve a predetermined operating temperature in the refrigerator chamber.

COOLERS OF DRINKS WITH WET CONTACT

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The paper presents the design of a new tabletop thermoelectric cooler with wet contact, i.e. with a gap filled with water between the container with the drink and the cooler chamber. The experimental test bench, test procedure and their results are described. The technical advantages of the new cooler are shown, in particular the increase in its speed of operation, which amounted to 15 to 65%. Found and described is the effect of accelerating the cooling of the drink when the temperature reaches 4 ° C associated with the inclusion of the second heat exchange mechanism - natural convection.

COMPUTER SIMULATION OF THE PROCESS OF CRYODESTRUCTION OF HUMAN SKIN DURING THERMOELECTRIC COOLING

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This paper presents the results of computer modeling of the process of cryodestruction of human skin, taking into account thermophysical processes, blood circulation, heat exchange, metabolic processes and phase transition. Physical, mathematical and computer models of human skin have been built, on the surface of which a cooling element at a temperature of -50 ° C is placed. The distributions of temperature and heat fluxes in human skin in the cooling mode are determined. The results obtained enable prediction of the depth of freezing of the skin and, accordingly, biological tissue at a given temperature.

Key words: human skin, temperature influence, cryodestruction, phase transition, computer simulation.

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