Thermoelectric Ceramic Element with Negative Temperature Factor of Resistance

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Abstract: The model of a thermoelement with branches from the materials, possessing in negative temperature factor of resistance is offered. The system of the equations describing the process of transferring heat and charge is received by the methods of the expanded irreversible thermodynamics. The results of calculations of the character of transferring heat and charge for various ratios of relaxation time are presented.

Keywords: thermoelement, thermistor, nanoceramics.

1. INTRODUCTION

A perspective direction in the field of working out of effective thermoelectric stuffs is building various nanostructures, such as quantum points, nanomoustache, super lattices, and volume nanocomposite [1]. The quantity of works, both theoretical, and experimental, devoted to research thermoelectric nanomaterial’s, recently is steadily growing, and, the received results are rather optimistically, at least, from the point of view of fundamental science.

Increase of thermoelectric quality factor in nonmaterials is connected with two physical phenomena [2]:

- The reduction of grid thermal conductivity is caused by occurrence of numerous borders of partition, that are effective centers of dispersion for phonons, but make small impact on electronic transport;

- Augmentation of width of the forbidden region with simultaneous augmentation of density of states near the Fermi level; although, in this case, electric conductivity decreases, but thermal e.m.f. increases that under certain conditions it can lead to increase of the vigor factor.

However, for creating of semi-conductor properties in nanocristaline ceramic materials of we can use the method of roasting in the recovery atmosphere [3-5]. Such method, together with usage of the materials with NTRC allows to raise efficiency of the thermal cells, especially in the field of high temperatures where ceramic materials, are the steadiest. It is possible to create both n - and p - phylum type of conductivity by selection of composition of gas atmosphere.

An elementary thermoelement is a basis of any thermoelectrical cooling device. It represents two semiconductor branches connected consistently, one branch possesses electronic conductivity (n), and the other possesses hole (p) conductivity. At the set current the value of temperature decrease depends on thermal load [2]. For increasing the figure of merit of a thermal element, the materials on the basis of telluride of bismuth is considered to be more perspective [3]. However, they have a narrow temperature gradient range and complexity in the production. Therefore, it is interesting to develop materials from conductive semiconductor ceramics based on interjacent metal oxides or composite materials [4]. That is why ceramic materials with a negative temperature coefficient of resistance (NTCR, - thermistors) [5-6] represent particular interest. Such materials can change conductivity value in wide ranges and it offers good prospects of their usage as materials of branches.

2. RESEARCH METHOD

The increase of the thermoelectric figure of merit in nanomaterials is associated with two physical phenomena [2]:

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- the decrease in the lattice thermal conductivity that appears in the nanomaterials of numerous boundaries, which are effective scattering centers for phonons, but which have little effect on electronic transport;
- the increase in the width of the forbidden band in nanomaterials, with the simultaneous increase of the density of states near the Fermi level; although in this case the electrical conductivity decreases, but the thermal EMF increases, and under the certain conditions it can lead to increasing of the power factor. It is possible to create both n- and p-type conductivity by selecting the composition of gas atmosphere.

With the help of the valence-controlled process, oxide ceramic materials can be transferred to the semiconductor state. For this purpose, different methods are used. For example, the recovery method: firing of ceramics in reducing ambient of non-isovalent substitution. In this case, it is possible to obtain an acceptable conductivity, while maintaining a low thermal conductivity. In ceramic materials one can enhance the scattering mechanism at low thermal conductivity, and it leads to the increase of the figure of merit [2].

\[
z = \left[ \frac{\alpha_1 - \alpha_2}{\sqrt{\chi_1 \rho_2} + \sqrt{\chi_2 \rho_1}} \right]^2
\]  

Where \( \alpha_1 \) and \( \alpha_2 \) are thermoelectric coefficient, \( \chi_1, \chi_2 \) are thermal conductivity coefficient, \( \rho_1, \rho_2 \) are resistivity of thermoelements branches.

In thermoelectric nanocomposites, the grain size does not exceed several tens of nanometers. To increase the thermoelectric efficiency, it is necessary to fulfill the following condition: the grain size should be smaller than the phonon path length but larger than the mean free path of the charge carriers (electrons or holes).

In nanocomposites it is obvious when the grain size decreases the fraction of the grain boundaries will increase, it will lead to a gradual decreasing of the thermal conductivity of the material. Naturally, the scattering of electrons at the grain boundaries will take place, and their mobility will be decreased. However, the decreasing of thermal conductivity in the bulk nanocomposites may be more significant than the decreasing of electrical conductivity. Thus, the bulk nanocomposites that consist of nanoscale grains of the thermoelectric material separated by typical grain boundaries can potentially have a high thermoelectric figure of merit, as they will have both high electrical conductivity and low thermal conductivity at the same time. Therefore, the usage of the materials with NTCR as the nanocomposite branches makes it possible to create a thermoelements with essentially nonlinear properties [6].

For example, in the case of isomorphous substitution, the number of spinels goes into the state of semiconductor conductivity with NTCR. Lithium doping of nickel oxide in the spinel leads to sharp increasing of conductivity due to the replacement of lithium ions into nickel ions in the octahedral positions. The formation of the solid solution with the uncompensated charge allows the variation of the lithium concentration to create a different type of conductivity [6].

**Figure 1.** Typical resistance dependence on the temperature for a thermistor with NTCR.
thermoelectric effect has a nonlocal character both in the coordinate and time.

An extended irreversible thermodynamics is one of the most consistent and detailed thermodynamic theories [8] that isn’t based on the principle of local equilibrium and takes into account spatial nonlocality of transport processes. In addition to the classical independent variables used by the local-equilibrium thermodynamics of irreversible processes, extended irreversible thermodynamics uses independent variables of dissipative flows, in our case it is a heat flux q and a charge flux I, to describe the state of the system far from the local equilibrium.

Thus, in the locally nonequilibrium system, S entropy is a function of both classical variables and dissipative flows:

\[ S = S \{ U(x, t), v(x, t), C(x, t), q(x, t), I(x, t) \} \]  

(5)

It should be noted that from the physical point of view, the new variables significantly differ from the classical ones. If the classical variables obey the laws of conservation and change relatively slowly during the evolution of the system, then the streams don’t obey the laws and are relatively "fast" variables, which rate of change can be high when the system is relaxed to local equilibrium. The introduction of the flows as independent variables is completely justified from the physical point of view. Indeed, if there is any flow in the system, this means a directed movement of the heat carriers or charges, i.e. such system is more ordered compared to a system where there are no such flows. Consequently, the entropy, which is known to be a measure of "disorder", must be less than the entropy in the system without the flows. Using the extended set of independent variables in the definition of locally- nonequilibrium entropy (5) and the classical formulation of the second law of thermodynamics with allowance for new locally-nonequilibrium terms in the expressions for the production of entropy and its flow, extended irreversible thermodynamics leads to differential equations for dissipative flows of evolutionary (relaxation) type:

\[
q + \tau_T \frac{\partial q}{\partial t} = -\lambda \nabla T - l^2 \nabla^2 q , 
\]

(6)

\[
\tau_e \frac{\partial i}{\partial t} = -(i - \sigma_e E') ,
\]

(7)

where \( E' = E - \nabla(T^{-1} \mu_e) \), \( \tau_T, \tau_e \) is the relaxation time of warmth and charge, \( l \) is the reference length of nonlocality , \( \sigma_e \) is conductivity, \( \mu_e \) is the chemical potential, \( \lambda \) is the thermal conductivity coefficient, \( E \) is the electric field strength, \( T \) is temperature.

Thus, the inclusion of dissipative flows in the series of independent variables leads to the fact that these flows are no longer determined by the gradient of the corresponding transfer potential, as in the
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classical local-equilibrium case, but they are solutions of the evolution equations (6 - 7). These equations describe the process of relaxation of dissipative flows to their local-equilibrium values.

While analyzing the system of equations (6 - 7), we use the following approximations. We assume that the coefficient of thermal conductivity and the relaxation time of the heat are constant and temperature is independent. Such assumption is correct in connection with the fact that the calculation of the heat relaxation time must be carried out taking into account the propagation of heat in the system. In other words, in the case of the heat propagation, the problem is self-consistent. Taking into account that the distribution of the heat and charge front may be considered in a single grain, we can assume that the spread of non-locality is rather weak, and the process describes the approach of the permanetand.

The $\tau_e$ - is an expression for the relaxation time of conduction electrons of a non-degenerate atomic semiconductor $\tau_e=\varepsilon^{1/2}/T$ [9], where $\varepsilon$ is an energy of the width order of the forbidden band of the semiconductor. Such an expression for the charge relaxation time is an approximation that has temperature dependence. It is necessary to solve the kinetic equation for the charge propagation taking into account the dispersion law in the conduction mechanism [9]. However, in our case, such task is complicated by the fact that it is necessary to consider the flow of the charge along the grain surface. It complicates the solution of the kinetic equation, which must be solved taking into consideration the percolation flow model.

It is usually assumed that the chemical potential doesn’t depend on temperature and is approximately equal to the Fermi energy. However, for a nondegenerate semiconductor with a temperature conductivity dependence (2), essentially nonlinear, it is necessary to take into account the temperature dependence of the chemical potential [10], which has a logarithmic temperature dependence:

$$\mu_e = kTln[\frac{4}{3\sqrt{\pi}}\left(\frac{\varepsilon}{kT}\right)\frac{3}{2}] < 0 \quad (8)$$

Where $k$ is a Boltzmann constant.

Thus, the problem of calculating the heat transfer in this system is nonstationary. To solve it, we assume the model to be one-dimensional, and dismiss the second-order terms in the temperature gradients. The initial and boundary conditions are assumed to be standard [7]. Such assumptions allow us to make a qualitative analysis of the nature of the propagation of heat and charge in the system. We examine the model at the distances of the grain size order. The generalization of the sample dimensions requires the establishment of an averaging procedure, which differs from the standard method i.e. the introduction of certain average or effective parameters requires additional considerations and cannot be carried out by simple averaging.

3. RESULTS AND DISCUSSION

The results of numerical simulation are shown in Figure 3. The system analysis (6-7) was carried out for various relations $\tau_T/\tau_e$ and the dimensionless time $t/\tau_T$ was used.
Figure 2. Propagation of heat in a thermoelement for various ratios $\tau_T$, $\tau_e$, $L$.

The result of the simulation is presented on figure 3a, provided that the times of relaxation of heat and charge are close. In this case, the propagation of heat occurs almost simultaneously with the charge density. It has a character close to a solitary wave. Such result is quite obvious, since in this case Joule heat is released simultaneously with heat transfer and the increase of the charge current occurs with the velocity that is close to the velocity of propagation of heat $V_1$. A characteristic feature of such propagation is a formation of the wave on the length of the conductivity hop.

In the case when there is $\tau_T >> \tau_e$ (figure 3b), the break of propagation front happens and the Joule heat wave $V_2$ outpaces the actual heat transfer wave due to the temperature gradient. Thus, in this case two waves are formed, which are spatially separated. At the same time, the relaxation of the heat does not occur during the hopping of the charge, and the system is in a locally nonequilibrium state. In other words, charge transfer generates a locally nonequilibrium state in which the charge flow is a fast variable.

In the case when there is $\tau_T << \tau_e$ (figure 3c), the heat relaxation occurs faster than the charge transfer, and a heat propagation front coinciding with the charge transfer is formed. It should be noted here that the steepness of the front is determined by the mechanism of hopping conductivity and the approximations in the calculation. When there is more correct calculation there will be no gaps on the front.

The mode of heat transfer will be especially manifested in functional gradient materials [3], especially along the grain boundaries. By creating a regular structure with the required relaxation time ratios, it is possible to achieve the wave character of the heat transfer and charge transfer. It will allow to create devices that simultaneously measure and regulate the temperature.

Investigating movement of a charging and temperature wave it is possible to estimate the relation of times of a relaxation. It will allow, at qualitative level to draw certain conclusions about the carrying over mechanism. Such possibility is very actual for ceramic materials.
4. CONCLUSION

The local-nonequilibrium process of heat and charge transfer in this paper can be realized in the branches of semiconductors the materials of which have got a negative coefficient of resistance. First of all, this is due to the essentially nonlinear dependence of the conductivity on the temperature. The determination of the quality factor of such a structure is a separate task, since it is necessary to calculate the thermo electromotive force, within the taken assumptions made. In contrast to conventional semiconductors, it should be taken in consideration the kinetics of charge and heat transfer. In this case, it is necessary to take into account the structure of the branch material and the mechanism of heat dissipation.

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AUTHORS’ BIOGRAPHY

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