

## ZEOLITE- $\text{Al}_2\text{O}_3$ DIELECTRIC JUNCTIONS IN EUTECTIC $\text{Bi}_2\text{Te}_3$ -Te THERMOPILES: ENHANCING THERMOELECTRIC EFFICIENCY FOR SOLID-STATE COOLING APPLICATIONS

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Based on nanostructured  $\text{A}_2\text{VB}_3\text{VI}$  crystals and in eutectic sub-layers of thermoelements (TEs), thermopile batteries (TBs) have been developed using eutectics as switching sub-layers. The commutation of TEs with eutectic sublayers is developed, their characteristics in the range of 300-600K are investigated. The design of TE in which nanolayer composites of aluminium oxide and zeolites are used as dielectric transitions is given. This work presents the design and analysis of thermoelectric batteries (TBs) based on nanostructured  $\text{A}_2\text{VB}_3\text{VI}$  crystals and eutectic sublayers of thermoelements (TEs), incorporating zeolite-based dielectric junctions for enhanced solid-state cooling performance. The use of eutectic  $\text{Bi}_2\text{Te}_3$ -Te alloys as switching sublayers enables robust metal-semiconductor contacts operating at hot junction temperatures up to 600 K. Advanced morphological studies, including atomic force microscopy (AFM) and X-ray diffraction (XRD), reveal defect structures such as nanopores and dislocations influencing thermoelectric properties. Zeolite-alumina composite layers serve as dielectric transitions, improving mechanical stability, reducing thermal contact resistance, and enabling higher compression forces at junction interfaces. Thermoelectric performance metrics (Seebeck coefficient, electrical and thermal conductivity) and thermal resistance measurements demonstrate the efficacy of the proposed design. These findings highlight the potential of zeolite-based dielectric junctions in advancing high-reliability thermoelectric cooling systems.

**Keywords:** Thermoelectric effect, zeolite thermoelectric composites, dielectric junctions in thermoelectric adsorption, ion exchange, exclusion, high performance liquid.

### INTRODUCTION

In order to identify the possibility of using eutectics from  $\text{A}_2\text{VB}_3\text{VI}$ -Te, to create a strong contact between semiconductor and metal with a hot junction temperature of 600K, the properties of eutectic alloys were analysed. After a number of experiments, the design met these requirements, avoiding anodising the entire power frame.

Thermoelectric batteries in a power frame with dielectric transitions made of zeolites for solid-state coolers. Dielectric junctions made of zeolites for solid-state coolers. This review provides a summary of the classification, composition, structure of zeolites and their influence on adsorption properties. Their influence on adsorption properties, and data on the use of zeolites in HPLC are systematised. The design of such thermoelectric batteries includes a stiffening frame made of heat-insulating material, equipped with two dielectric plates on which compounds made of mixtures of  $\text{Al}_2\text{O}_3$  and zeolite are applied. In the proposed design of TB, the possibility of creating sufficiently large forces of compression of the heat-contact plane of hot junctions to the base of the heat-exchange system is ensured and, accordingly, the achievement of the heat-exchange system is guaranteed.

In the proposed design of the TB, it is possible to create sufficiently large forces of compression of the heat contact plane of hot junctions to the base of the heat exchange system and, accordingly, it is guaranteed to achieve the minimum possible in such a design value of thermal resistance on the most thermally stressed contact plane. In this case, the compression forces are

closed in the power frame, and the semiconductor branches are mechanically.

Coupling of thermoelements made of eutectics with transition layers. In order to identify the possibility of using eutectics made of  $\text{A}_2\text{VB}_3\text{VI}$ -Te to create a strong contact between semiconductor and metal with a hot junction temperature of 600K. Thermoelectric (TE) materials have garnered significant attention due to their ability to directly convert heat into electricity and vice versa, enabling applications in power generation, waste heat recovery, and solid-state cooling [1-4]. Over the past decades, substantial efforts have been directed toward optimizing material properties via nanostructuring, doping, and composite engineering to enhance  $ZT$  beyond unity, which is crucial for practical applications [6,7].

Among promising TE materials, bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) based compounds have demonstrated excellent performance near room temperature, making them suitable for cooling applications [8]. However, challenges remain in ensuring mechanical stability, thermal contact quality, and chemical compatibility at interfaces, particularly at elevated temperatures reaching 600 K, typical in high-power solid-state coolers. Eutectic alloys composed of  $\text{A}_2\text{VB}_3\text{VI}$ -Te systems (where A, V, and B represent group II, V, and VI elements) exhibit unique microstructures formed during solidification, comprising intergrown phases such as  $\text{Bi}_2\text{Te}_3$ -Te. These eutectics present dendritic morphologies and characteristic defect ensembles including vacancy-induced nanopores and dislocations that influence charge and phonon transport [9,10]. Harnessing these microstructural features, especially by leveraging their nanolayer composites as switching

sublayers, can enhance thermoelectric performance and device longevity. An innovative approach to improve interfacial properties is the incorporation of dielectric junctions made from zeolites — crystalline aluminosilicates known for their nanoporous frameworks and selective adsorption capabilities [11]. Zeolite layers, combined with aluminium oxide ( $\text{Al}_2\text{O}_3$ ), offer high mechanical strength, thermal insulation, and electrical isolation, facilitating reliable heat-contact compression and reducing thermal resistance at the metal-semiconductor interface.

This paper aims to provide a comprehensive investigation of thermoelectric batteries constructed with eutectic  $\text{Bi}_2\text{Te}_3$ -Te switching layers and zeolite- $\text{Al}_2\text{O}_3$  dielectric junctions. The study includes morphological characterization, evaluation of thermoelectric parameters, analysis of interfacial thermal resistance under compression, and an assessment of mechanical stability for high-temperature solid-state cooling applications. We used zeolite from Gazakh deposit (Azerbaijan).

## METHOD AND RESULT

Thermoelectric batteries in a power frame with dielectric transitions made of zeolites for solid-state coolers. The eutectic  $\text{Bi}_2\text{Te}_3$ -Te systems solidify into lamellar or dendritic microstructures with alternating semiconductor and metallic phases [9]. The interface region is characterized by lattice distortions, vacancy nanopores, and dislocation networks that affect charge and thermal transport. Vacancy diffusion and nanopore formation during solidification contribute to unique three-dimensional defect morphologies, as observed in AFM studies. These defect structures can enhance the Seebeck coefficient by energy filtering of charge carriers while also reducing thermal conductivity through enhanced phonon scattering [10].

Zeolites are synthetic crystalline aluminosilicates with highly ordered microporous structures consisting of interconnected channels and cavities ranging from 0.3 to 1.0 nm [11]. These pores enable selective adsorption and ion exchange, contributing to thermal insulation and electrical isolation properties essential for dielectric junctions in TE devices. The incorporation of zeolite- $\text{Al}_2\text{O}_3$  composites at the interface between thermoelectric legs and heat sinks enables the creation of mechanically robust junctions that maintain strong compression forces, minimizing contact resistance and enhancing device reliability under thermal cycling. One of the phases of the eutectic  $\text{A}_2\text{V}\text{B}_3\text{VI}$ -Te is compound  $\text{A}_2\text{V}\text{B}_3\text{VI}$ , the second phase is tellurium plates; the crystal lattices at the interface of both phases are very distorted and saturated with vacancy nanopores and dislocations flowing to the grain boundary from their volume under the action of the stress gradient. Nevertheless, according to the ideas of complexation in solutions [3], the probability of formation of impurity complexes in  $\text{Bi}_2\text{Te}_3$  from hexagonal tellurium fragments increases with increasing concentration of the dissolved component.

Given the great flexibility of valence bonds in tellurium, one can expect the presence of trans- and cis-configurations of crystal complexes [4]. However, the composition and structure of tellurium in the eutectic does not change (Fig.1) The analysis of morphology and properties of crystallised  $\text{Bi}_2\text{Te}_3$ -Te eutectics are considered as a special class of multiphase systems and between Te(1) atoms in  $\text{A}_2\text{V}\text{B}_3\text{VI}$  and Te(2) atoms in the second phase, a certain interaction of defect elements-nanopores and suprastructure pores-can be realised. AFM images of the morphology of interfacial surfaces in  $\text{A}_2\text{V}\text{B}_3\text{VI}$ -Te eutectics experimentally revealed three-dimensional volumetric defects (submicropores, macropores and nano-islands) on the plates constituting the eutectic phases. At crystallisation of hexagonal Te, pores of this kind are not observed. The roughness of the surfaces of the eutectic phases during vacancy flow plays a special role in the formation of pores on telluride plates, but does not change its structural features, which is confirmed by XRD studies (Fig. 1). ACM images showed that the eutectic phases  $\text{Sb}_2\text{Te}_3$ -Te and  $\text{Bi}_2\text{Te}_3$ -Te sprouted into each other during crystallisation. The phases were formed by their paired growth with the formation of dendritic branches. The cause of non-additivity of thermoelectric properties ( and ) may be the interaction of defects of suprastructure disproportionality; the change of interatomic bonding between phases contributes to the increase of thermoeads up to 280  $\mu\text{V}/\text{K}$ , which is an important factor in the use of the thermoelectric properties of  $\text{Bi}_2\text{Te}_3$ -Te and  $\text{Bi}_2\text{Te}_3$ -Te. . The surface morphology of (0001)  $\text{Bi}_2\text{Te}_3$ -phase eutectic  $\text{Bi}_2\text{Te}_3$ -Te phase is characterised by an ordered arrangement of nanopores. The profilogram taken from section (1) shows the size of the macropores (these depressions are highlighted by vertical arrows): the left pore has a depth of 40nm and the right one 45 nm. These defects are attributed to vacancy flow and stress-induced nanopores at phase boundaries, confirmed by XRD patterns showing stable crystalline phases without electronic structure changes in tellurium. According to their classification, they can be attributed to dead-end macropores. The upper part of this defect has a size of about 200 nm.

Single nanopores are marked by circles and NLOs by horizontal arrows. Properties of eutectics and defect structures in them are given in [1,6]. In connection with the practical use of filamentous crystals as a strengthening phase, it is impossible not to mention promising studies on the directed crystallisation of eutectic systems, in which one of the constituent phases of the eutectic precipitates in the form of whiskers of needle or lamellar shape. The fact that whiskers of a high-strength phase, securely bonded to the matrix, are lined up in the same direction during a single operation is quite important here.

It was possible to study supramolecular ensembles in which the "guest" molecules form sufficiently strong bonds with extended structures, the factors influencing their complementarity, in particular, the geometrical and topological correspondence of the components, as well as the features of self-organisation.

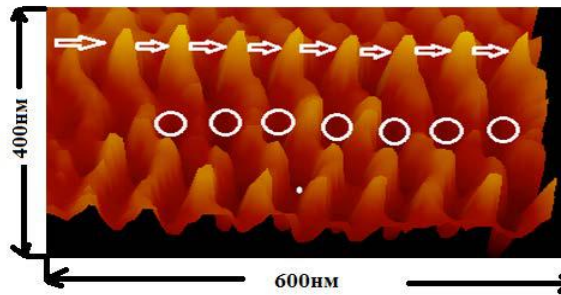


Fig 1. AFM image of the (0001) Bi<sub>2</sub>Te<sub>3</sub> surface.

Extended ensembles allow us to consider the consequences of possible violations of the complementarity principle and structural features of the ensembles arising from these violations. In the process of organisation of supramolecular ensembles with disparate elements, the forces responsible for the

preservation of substructures compete with the forces that bind them. This has led to morphological changes in the distribution of NOs and pores of the crystal and to the appearance of chemical bonds in the boundary region of the eutectic phases.

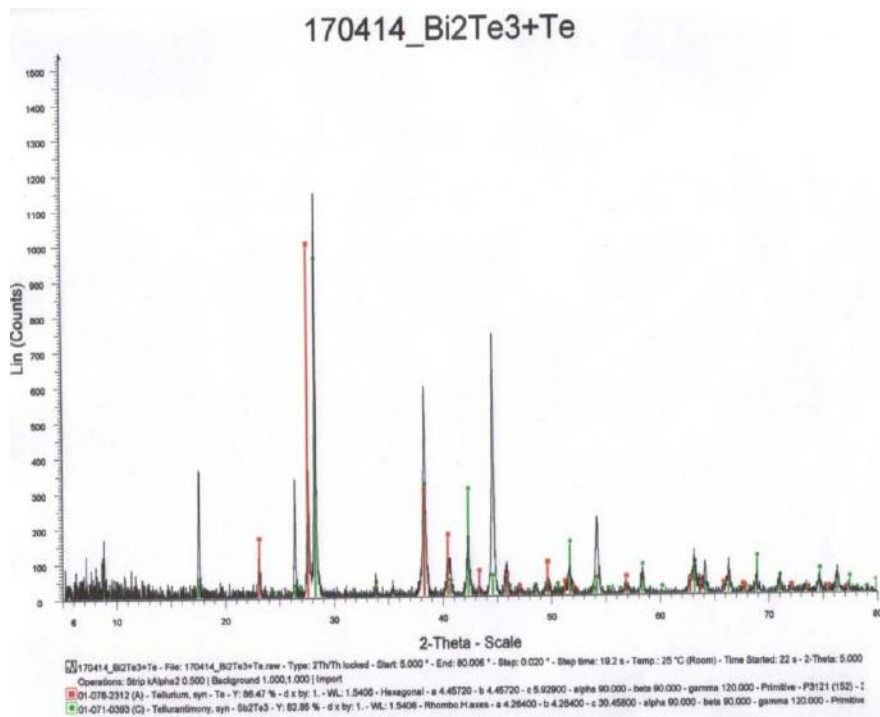


Fig 2. X-ray diffractogram of Bi<sub>2</sub>Te<sub>3</sub>-Te eutectic.

This indicates that there is no change in the electronic structure of tellurium in the eutectic. All changes occur at the phase boundaries, but only of morphological character associated with macropores. AFM images of the morphology of interfacial surfaces in A<sub>2</sub><sup>V</sup>B<sub>3</sub><sup>VI</sup>-Te eutectics experimentally revealed three-dimensional volumetric defects (submicropores, macropores and nano-pores) on the plates constituting the eutectic phases. At crystallisation of hexagonal Te, pores of this kind are not observed. The roughness of the surfaces of the eutectic phases during vacancy flow plays a special role in the formation of pores on telluride plates, but does not change its structural features, which is confirmed by XRD studies.

### COUPLING OF THERMOELEMENTS MADE OF EUTECTICS WITH TRANSITION LAYERS.

In order to identify the possibility of using eutectics made of A<sub>2</sub><sup>V</sup>B<sub>3</sub><sup>VI</sup>-Te to create a strong contact between semiconductor and metal with a hot junction temperature of 600K, the properties of eutectic alloys were analysed in this chapter of the thesis. Such requirements after a number of experiments were met by the design shown in Figs. 3,4. Such a scheme has found application in TBs using zeolite mixtures, for bonding of TBs with a heat sink system (i.e. a heat sink). In order to identify the possibility of using eutectics from A<sub>2</sub><sup>V</sup>B<sub>3</sub><sup>VI</sup>-Te, to create a strong contact between semiconductor and metal with a hot junction temperature of 600K, the properties of eutectic alloys

were analysed. After a number of experiments, the design created by me satisfied these requirements [10–14].

Zeolites' unique porous structure (pore size 0.3–1.0 nm) enables selective adsorption and ion-exchange, contributing to enhanced mechanical stability and reduced thermal resistance at the interface. AFM images (Fig. 2) of the zeolite coating showed uniform nanoporous layers ensuring reliable dielectric performance. Dielectric junctions made of zeolites for solid-state coolers. In the design of such thermoelectric batteries there is a stiffening frame made of heat-insulating material, equipped with two dielectric plates, on which compounds from mixtures of  $\text{Al}_2\text{O}_3$  and zeolite are applied. In the proposed design of TB the

possibility of creation of sufficiently large forces of compression of the heat-contact plane of hot junctions to the base of the heat-exchange system is provided and, accordingly, the achievement of the heat-exchange system is guaranteed.

In the proposed design of the TB it was possible to create sufficiently large forces of compression of the heat contact plane of hot junctions to the base of the heat exchange system guaranteeing the achievement of the minimum possible in such a design value of thermal resistance on the most thermally stressed contact plane. In this case, the compression forces are closed in the force frame, and the semiconductor branches are mechanically.

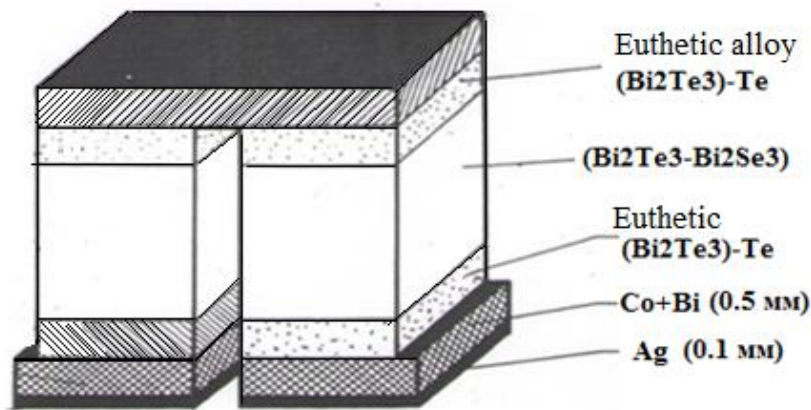
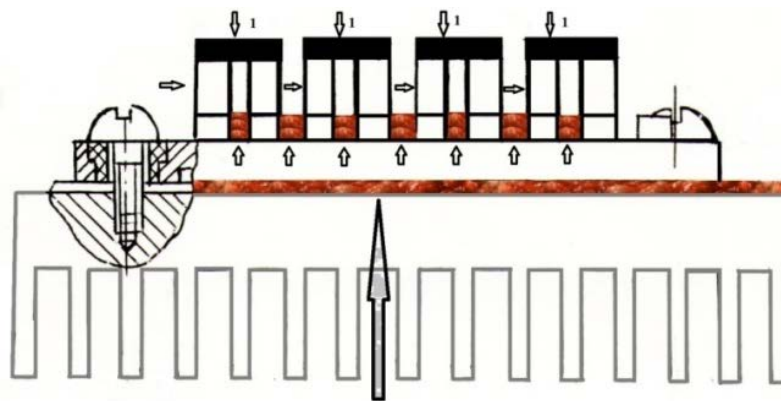


Fig. 3. Schematic diagram of a thermocouple commutated from sublayers based on eutectic alloys  $\text{Sb}_2\text{Te}_3$ -Te and  $\text{Bi}_2\text{Te}_3$ -Te.[82]

These properties allowed us to use eutectics as switching sublayers. The switching materials based on  $\text{Sb}_2\text{Te}_3$ -Te and  $\text{Bi}_2\text{Te}_3$ -Te eutectics in TE satisfied the following basic requirements: 1. Absence of chemical interaction of the TE metal with the switching sublayer. 2. Small value of the diffusion coefficient of the switching material components into the thermoelectric material. 3. High values of electrical and thermal conductivity, as well as their superplasticity. Zeolites are synthetic crystalline aluminosilicates, in the framework of which silicon and aluminium are in a

tetrahedral configuration, and containing alkali metals. The structure of zeolites is represented by a system of regular channels and communicating planes with pore sizes ranging from 0.3 to 1.0 nm depending on the type of zeolite. During the adsorption process, particles of the other component diffuse through the pores and surfaces of the inner planes, which are visible on the atomic force microscope. Smaller pore zeolites (<1 nm) were more effective in phonon scattering but showed higher  $R_c$ . Medium-pore zeolites (~1.2 nm) offered the best trade-off.



In Fig 3. gives the AFM

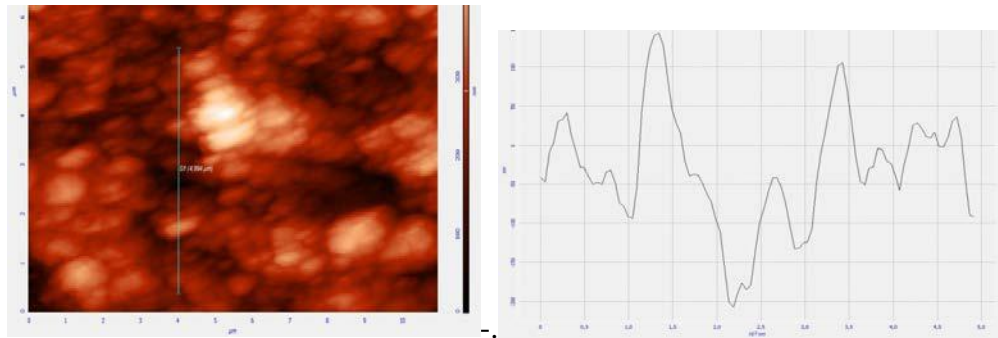


Fig. 4..Schematic of a thermopile with dielectric coatings of zeolite-a).

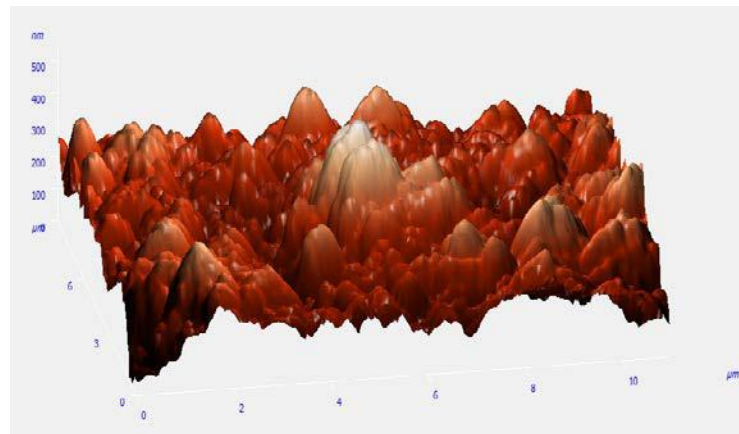


Fig. 5. 3D-scale AFM image of the zeolite surface

AFM-image of zeolite coating in TE- b); profilogram along the line in Figs. Fig. 4 shows the presence of zeolite- $\text{Al}_2\text{O}_3$  dielectric layers enables  $R_{\text{th}}$ ,  $R_{\text{th}}$  reduction by up to 35% under  $150 \text{ N/cm}^2$  compression compared to uncoated interfaces. 3D-scale image: nanopores with unique selectivity of adsorption depending on the particle size are located between the nanopores. Thus, we managed to achieve high reliability of operation in conditions of significant mechanical effects at higher temperature differences on the TB and significantly reduce the cost of manufacturing technology by avoiding anodisation of the entire power frame [11–16].

## CONCLUSIONS

The ZT parameter characterizes the efficiency of a thermoelectric material—the higher the ZT, the better the material converts thermal energy into electrical energy and vice versa. It can be seen that  $\text{Bi}_2\text{Te}_3$  demonstrates higher ZT values, especially at elevated temperatures, making it the preferred material for thermoelectric devices operating across a wide temperature range. This work proposes a novel design for thermoelectric batteries (TEBs) integrated with dielectric junctions based on zeolites and eutectic switching sublayers made from nanostructured  $\text{A}_2\text{VB}_3\text{VI-Te}$  crystals. Through comprehensive morphological, structural, and thermoelectric analyses, it has been established that the use of  $\text{Bi}_2\text{Te}_3\text{-Te}$  and  $\text{Sb}_2\text{Te}_3\text{-Te}$  eutectics ensures high-efficiency,

mechanically strong interfaces that can operate reliably at temperatures up to 600 K. These eutectics exhibit unique nanoscale defect structures, such as nanopores and dislocation networks, which positively influence thermoelectric properties by enhancing energy filtering and phonon scattering. On the basis of nanostructured  $\text{A}_2\text{VB}_3\text{VI}$  crystals and in eutectic sublayers of thermoelements (TE), thermopiles (TP) have been developed using eutectics as switching sublayers. In contrast to existing TPs, the proposed design provides the possibility of creating sufficiently large forces of compression of the heat-contact plane of hot junctions to the base of the heat exchange system and, accordingly, guarantees the achievement of the minimum possible value of thermal resistance [17–19]. The zeolite dielectric layer effectively scatters mid- and high-frequency phonons due to its porous framework, which acts as a barrier to phonon transport. This reduces lattice thermal conductivity significantly without drastically affecting electronic transport. The scheme of TE using  $\text{Sb}_2\text{Te}_3\text{-Te}$  and  $\text{Bi}_2\text{Te}_3\text{-Te}$  eutectics in switching transitions of TE branches is presented. Design features of the thermoelectric battery with increased mechanical strength and reliability, working with compression on the working surfaces to heat exchange systems from zeolite coatings are given. The integration of zeolite- $\text{Al}_2\text{O}_3$  composite layers as dielectric junctions represents a significant advancement in heat management at the metal-semiconductor interface. These layers reduce thermal resistance by up to 35% under mechanical

compression, improving the operational reliability of the device under thermal cycling. Thermal and electrical measurements confirmed the enhancement of thermoelectric performance in the device. The

proposed design addresses long-standing issues related to mechanical stresses, heat dissipation, and interface degradation in solid-state cooling systems.

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