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Thermoelectric properties of the metallic nanoclustered model material

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Thermoelectric properties of the metallic nanoclustered model material.

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Abstract. In this work the Seebeck coefficient of simple model of nanoclustered material with respect to bulk form was investigated. The first-principle calculation of Seebeck coefficient of the bulk and model nanoclustered form of Ta was performed via semiclassical Boltzmann transport approximation with constant relaxation time, using first-principal bandstructure calculated in density functional theory. 5-15-times increasing of Seebeck coefficient was estimated for simple model of nanoclustered material.

1. Introduction

Nowadays challenges of modern energetics demands the high effective thermoelectric materials. The efficiency of thermoelectric generation in thermoelectric material is expressed by the dimensionless value figure of merit $ZT=S^2\sigma T/k$. Here S is the thermoelectric power (Seebeck coefficient), σ is the electrical conductivity, and $k = k_{el} + k_l$ is the thermal conductivity, composed of electronic and phononic parts. One can see from ZT expression, that it can be increased mostly by increasing S, then σ, and decreasing κ. Improving the ZT of traditional high-S thermoelectric materials (such as $CsBi_4Te_6$, Bi_2Te_3, Sb_2Te_3) by doping, alloying, layer composing have been successful till recent time, but effectiveness of this way is limited [1-4]. Another way is to decrease thermal conductivity k by the disordering or clusterisation: it is expected that phoninic transport will be restricted in structure made from disordered localized nanoparticles but electronic conductivity will be provided by percolation effects [1]. But for semiconductors further increasing ZT by diminish the particle size is limited due to the fact of critical degradation of electric conductivity of semiconductor nanoparticles with decreasing their size [5,6]. On the other hand, it was observed for metal nanoclusters, that it stay conductive down to ~1nm size and manifestation of semiconductor properties at lower sizes [7]. Moreover in experiment [8] it was estimated that S of d-metallic nanoclusters with volume decreasing lower than $1nm^3$, appears 10 times higher than S of corresponding bulk sample. Summarizing these facts we can presume, that disordered, porous structures composed of metallic nanoclusters, can be promising materials for high-efficiency thermoelectric elements. The thermoelectric properties generally depend on electronic properties in the complex law, which can be simply approximate by Mott's law for simple metals. It shows how the conductivity σ and thermopower S depends on the electronic density of states (DOS) features near the Fermi energy E_f (the steeper the DOS the higher is S), occupation at E_f, band structure features and anisotropy effects on S and σ directly too. So, information about electronic structure helps to predict the thermoelectric properties. On the other hand we can construct the structures of nanoclusters with especial electronic propertie, because its size, geometry and electronic structure are interdependent.

In this work we investigate how the "clusterization" or slight disordering effects on Seebeck coefficient with respect to bulk form. We consider the simplest model of metallic nanoclustered material: simple cubic lattice formed by small nanoclusters. For the reasons mentioned above, d-metals have proper electronic structure, with highly localized d band, spin-orbit splitting, and mostly high conductivity. But for the complex electronic structure of the d-metals the simple analytical electronic-thermoelectric approximations is inappropriate. For first-principle thermoelectric coefficients calculation we use the semiclassical upproach Boltzmans equations in constant relaxation time approximation with tensor coefficients derived directly from electronic band structure E_i ($\mathbf{k}_j$) (bolzttrap algorithm) [9]. Bands data is obtained via density functional theory calculations on large set of **k**. Within this method obtain Seebeck coefficient S(T, μ), conductivity σ/τ(T, μ) where μ is the chemical potential, τ is the uncertain constant relaxation time. As soon as Seebeck coefficient is independent of τ value and $ZT{\sim}S^2$, we consider temperature dependence $S(T, \mu{\sim}E_{fermi})$ at several temperatures. Generally, nanoclusters melting temperature is lower than bulk [10,11], so we consider refractory d-metal Ta to safely consider temperatures up to 500 K, that corresponds to the range of thermoelectric elements usage. The calculated S(T) for bulk and nanoclustered model of Ta is compared.

2. Calculation methodic and results

Study of the electronic structure of bulk Ta was provided using density functional theory (DFT) method with pseudopotential in plane-wave basis set implemented in Quantum Espresso code [12]. DFT calculations was performed in generally-gradient approximation of the exchange-correlation energy (GGA PBE) including the spin-orbit interaction for the noncollinear spin orientation and nonmagnetic state. For the valence configuration of Ta (5s2 5p6 6s2 5d3) fully-relativistic ultrasoft Vanderbild pseudopotential with core correction uncluding semicore states in valence was used [13]. Self-consistent energy calculation was performed on 12x12x12 k-mesh with 750 eV plan wave kinetic energy cutoff. Electronic energy bands and density of states (DOS) calculations was performed on dense 48x48x48 Monkhorst-Pack k-mesh.

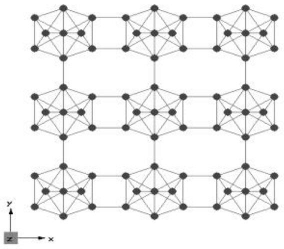

Fig. 1. Lattice of nanoclusters Ta_{13} model scheme.

It was investigated by molecular dynamic simulations that icosahedral Ta_{13} structure is the most energetic-preferable and stable form of the <1nm nanoparticles [14]. Let's consider the simple cubic superlattice composed of small ~0.5nm Ta_{13} nanoclusters (see Fig.1). Structure relaxation was performed with embedded atom model potential [15] and force threshold of 0.05 eV/A. Superlattice parameter or intercluster distance was defined by this procedure in order to save ability of appearance new bends, but to avoid total disordering by interatomic forces and save icosahedral units. It was provided purposely to investigate structure with controlled (parametrized) disordering, as first step of disordering simulations. Thus the global symmetry became decreased only two times with respect to the ordinary bulk lattice (24vs48 translation operators). Then DFT self-consistent and band structure calculation was performed using the former parameters.

The semiclassical Seebeck coefficient S(T, μ=Ef) was obtained from DFT bandstructure $E_i(\mathbf{k}_j)$ for T = 100-500K for bulk and model nanoclustered Ta. S(T) results compared with experimental is shown in Fig.1.

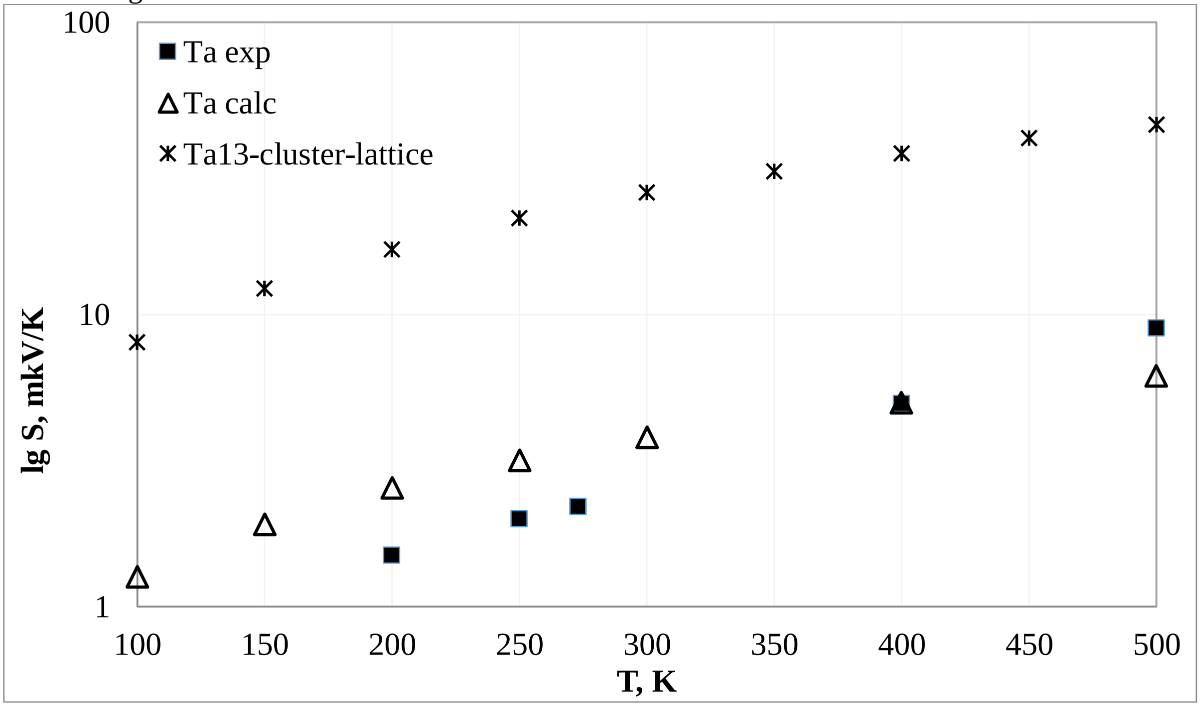

Fig. 2. Seebeck coefficient logarithmic dependence of temperature for Ta structures. Black squares marks experimental values of Seebeck coefficient S, white triangles – S calculated for bulk Ta. Stars marks calculated S for model lattice formed from Ta_{13} nanoclusters.

Fig.2. showed results of the S(T) calculation for bulk and model nanoclustered Ta material. The bulk S calculations show the best accuracy in T=250-400K range, the minimal declination with experimental one is 1% at 400K. One can see that in simple model of nanostructured material constructed by 0.5 nm Ta13 clusters, S value can grow by 5÷15 times with respect to bulk, at 300 K it appears 26 mkV/K. In the resent experimental research [16] the thermopower of the film, formed from 1.3 nm Ta clusters, was indirectly measured and it found to be about 15 mkV/K at room temperature. That proves the results of current study.

Thus ab initio calculations of the thermopower of nanoclustered metal, presented by simple model of sulerlattice formed from small nanoclusters Ta_{13}, showed that Seebeck coefficient appear to be 5~15 times higher than bulk metal. We suggest that more disordered structure, formed from nanoparticles of larger and different sizes, can be more thermoelectrical effective, having higher S and lower k for the reasons recently studied.

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