INVESTIGATION OF PHONON SUPPRESSION BY NANOSTRUCTURING AND DOPING IN THERMOELECTRIC HALF-HEUSLER MATERIALS

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Abstract

We live in the age when humanity finds itself on the edge of energy crisis, fossil fuels are consumed and our energy consumption rises every year. One solution would be to obtain energy from renewable sources and to minimize the losses of energy produced, e.g. reuse the waste heat. Thermoelectric materials can convert heat directly and reversibly into electricity and allow therefore to use waste thermal energy more efficiently. Their benefits include the absence of moving parts, quiet operation, reliability, durability, and the fact that they do not produce any polluting emissions, so we can use them in a wide range of applications and they are also attractive from an environmental point of view. Half-Heusler alloys belong to one of the most promising thermoelectric materials composed of relatively non-toxic and abundant elements, with highest ZT = 1.5 at 700 K for $Zr_{0.25}Hf_{0.25}Ti_{0.5}Ni_1Sn_{0.998}Sb_{0.002}$ at% alloy. In our study we try to improve the thermoelectric performance of this alloy by doping it with semiconducting dispersion phase - β-$FeSi_2$, which should reduce the thermal conductivity of the origin alloy. Since thermal conductivity depends to large extent on the propagation of phonons we have investigated how the nanostructuring of the samples by means of ball milling and doping impact the phonon behavior. For this purpose we have conducted inelastic neutron scattering experiments using the time-of flight spectrometer NEAT at Helmholtz Zentrum Berlin. In this paper are presented results of our study demonstrating the effect of phonon suppression by nanostructuring and doping in thermoelectric half-Heusler alloys.

Keywords: Thermoelectric materials, phonons, half-Heusler alloys, inelastic neutron scattering

1. INTRODUCTION

Thermoelectric materials have been extensively studied because of their huge potential in waste heat recovery and refrigeration industry [1]. They can convert temperature gradient in to electricity and vice versa. The efficiency of this process is summarized by the dimensionless figure of merit

$$ZT = \frac{S^2\sigma}{\kappa}T \quad (1)$$

where:

S - the Seebeck coefficient (μV/K),

σ - the electrical conductivity (S/m),

κ - the thermal conductivity (W m^{-1} K^{-1}),

T - the absolute temperature (K).

From equation (1) is obvious that for increase of ZT we have either to increase the numerator $S^2\sigma$ (the power factor) or to decrease κ. All three parameters S, σ, κ are strongly connected. The σ parameter depends on number of the free charge carriers. The thermal conductivity κ is combination of two terms - electrical κ_e (heat

transported by charge carriers) and lattice thermal conductivity κ_L, where heat is transported through crystal lattice by form of lattice vibrations - phonons. The κ_e *parameter* is interconnected to the σ by Wiedemann-Franz law [2] and therefore in praxis the reduction of κ is realized only by decreasing κ_L. From the kinetic theory, the lattice thermal conductivity can be estimated as

$$\kappa_L = \frac{1}{3} C v_m l \quad (2)$$

where:

C - the lattice specific heat (J/K),

v_m - the mean sound velocity (m/s),

l - the mean free path of the phonons (m).

There are several approaches to reduce κ_L by means of reducing l (scattering of the phonon waves): nano-structuring [3], alloying [4], and guest atom inclusion [5]. Particularly powerful method used for studying phonons is inelastic neutron scattering.

The aim of the presented work was to develop a new thermoelectric material with high conversion efficiency, which would consist of non-toxic, inexpensive and affordable elements. Therefore, we decided to produce a half-Heusler (HH) alloy: $Zr_{0.25}Hf_{0.25}Ti_{0.5}Ni_1Sn_{0.998}Sb_{0.002}$ at.%, which achieves ZT_{max} = 1.5 at 700 K [6]. To decrease lattice thermal conductivity we introduce nanostructuring of the sample by means of high energy ball milling and spark plasma sintering (sample HH0). For further lowering of κ_L we have doped this alloy with a semiconducting dispersion phase β-$FeSi_2$ in the form of 2 vol% (sample HH1). Inelastic neutron scattering experiments were performed to understand lattice dynamics - phonon behavior of nanostructuring and doping effects on HH samples. To compare temperature dependent phonon density of states (DOS) of ball milled HH0 sample and doped sample HH1, we measured also the alloy in well relaxed state, prepared by arc-melting and annealed in furnace at high temperature (sample HH00). For better clarity, chemical compositions and preparation processes of each sample are summarized in **Table 1**.

Table 1 Thermoelectric HH samples

Name	Chemical composition	Preparation methods
HH00	$Zr_{0.25}Hf_{0.25}Ti_{0.5}Ni1Sn_{0.998}Sb_{0.002}$ (at%)	Arc-melting: 3x, Annealing 3 h at 800 °C in protective atmosphere
HH0	$Zr_{0.25}Hf_{0.25}Ti_{0.5}Ni1Sn_{0.998}Sb_{0.002}$ (at%)	Arc-melting: 3x, Ball milling: 1 h in protective atmosphere, SPS
HH1	$Zr_{0.25}Hf_{0.25}Ti_{0.5}Ni1Sn_{0.998}Sb_{0.002}$ (at%) + 2 vol% β-$FeSi_2$	Arc-melting: 3x, Ball milling: 1 h in protective atmosphere, SPS

2. MATERIALS PREPARATION

All HH samples were prepared from elements of high purity: Zr (99.2 %), Hf (99.7%), Ti (99.99%), Ni (99.98%), Sn (99.9%), Sb (99.9999%), Fe (99.98%), Si (99.9999%). After proper weighting, samples were arc-melted, at least 3 times to ensure homogeneity, in the Edmund Bühler - Compact Arc Melter MAM-1 using maximum power of the device. Additionally, HH00 was annealed for 3 hours at 800 °C in tube furnace in order to reduce the residual stresses formed by rapid cooling in arc-melting process. HH0 and HH1 ingots were firstly crashed, then pre-milled in vibration mill and finally ball milled under Ar atmosphere for 1 hour at 200 RPM in planetary ball mill - FRITSCH PULVERISETTE 6. Prepared powders were compacted by spark plasma sintering (SPS) at temperature 1473 K under pressure 16 kN for 10 minutes using 20 mm graphite dies in - SPS HP D10-SD. Obtained compacts (pellets) were then cleaned from graphite and polished.

3. NEUTRON SCATTERING EXPERIMENTS

In order to determine thermal dynamics of the HH samples, inelastic neutron scattering (INS) experiments were performed. All 3 HH samples were measured at the NEAT time-of-flight (TOF) spectrometer - V3 beamline located at Helmholtz-Zentrum Berlin (HZB). HZB is operating a swimming-pool fission reactor BER II. with cold source of 10 MW power.

3.1. NEAT Spectrometer

NEAT is a chopper system TOF spectrometer. Neutrons are generated in cold source reactor and then travel a long distance of 64 m to the sample. On their way through neutron guide they pass seven rotating discs choppers with small openings, which function is to cut neutrons of desired wavelength (λ_0) from continuous energy spectrum of the reactor. Second important function of choppers is, that they create a well-defined time pulses of neutrons, what is necessary for the TOF technique. Monochromatic neutron pulses then hit the sample and are scattered to detector. The sample to detectors distance is constant 3 m. NEAT is composed of 416 $^{3+}$He radially placed detectors covering scattering angles from 142° to - 82° [7]. With known distances between pulse creating chopper - sample - detectors and with fixed λ_0, we are now able to measure TOF of neutron scattered on the sample. Scattered neutrons arrive at the detectors at times determined by their scattered energies E. Therefore we can calculate neutron energy transfer $\hbar\omega = E_0 - E$, which in our energy range represents the phonons. Given the angle between the incident ($\boldsymbol{k_0}$) and scattered neutron wave-vectors ($\boldsymbol{k}$), i.e. the scattering angle Φ, the wave-vector transfer $\boldsymbol{Q} = \boldsymbol{k_0} - \boldsymbol{k}$ is readily calculated. Measuring the intensities of time and angular scattered neutrons we can calculate a neutron scattering function $S(Q,\omega)$ or more precisely dynamic structure factor [8].

4. EXPERIMENTAL PART

4.1. Instrumental setup

Each HH sample was loaded into a flat Al sample holder (SH) and placed to cryostat installed inside in the detector chamber. Upper part of the SH was covered by Cd shielding in order to reduce Al intensity as much as it was possible. Because we want to use full cross section of the neutron beam at the sample (2 x 6 cm), we decided to cut the disc samples along and place them on each other like „8“, to cover more space. Sample HH00 (not SPS-ed) in form of round ingot was not cut. All 3 samples: HH0, HH1 and HH00 were measured at neutron wavelengths: 2, 3, and 5 Å by temperatures: 100, 200, 300, 400 K. At the same conditions empty SH (empty can) and also Vanadium standard were measured.

4.2. Data treatment

For data processing we have used MANTID software. Best resolution of phonon branches we obtained by using 0.3 nm wavelength, so in further calculations only this energy data will be used. Because measured samples had different scattering intensity, samples HH00 and HH1 were normalized to weight of the sample HH0.

5. RESULTS AND DISCUSSION

The first insight of nanostructuring effect we observe by investigation of elastic part of the spectra. In **Figure 1**, there are presented elastic neutron spectra of all the 3 HH samples measured at the temperatures 100, 200, 300 and 400 K. On spectra from the HH0 and HH1 samples we do not observe Bragg reflection (200). Suppression of the (200) peak can be attributed to effective nanostructurization of the origin alloy caused by high energy ball milling process - samples HH0 and HH1.

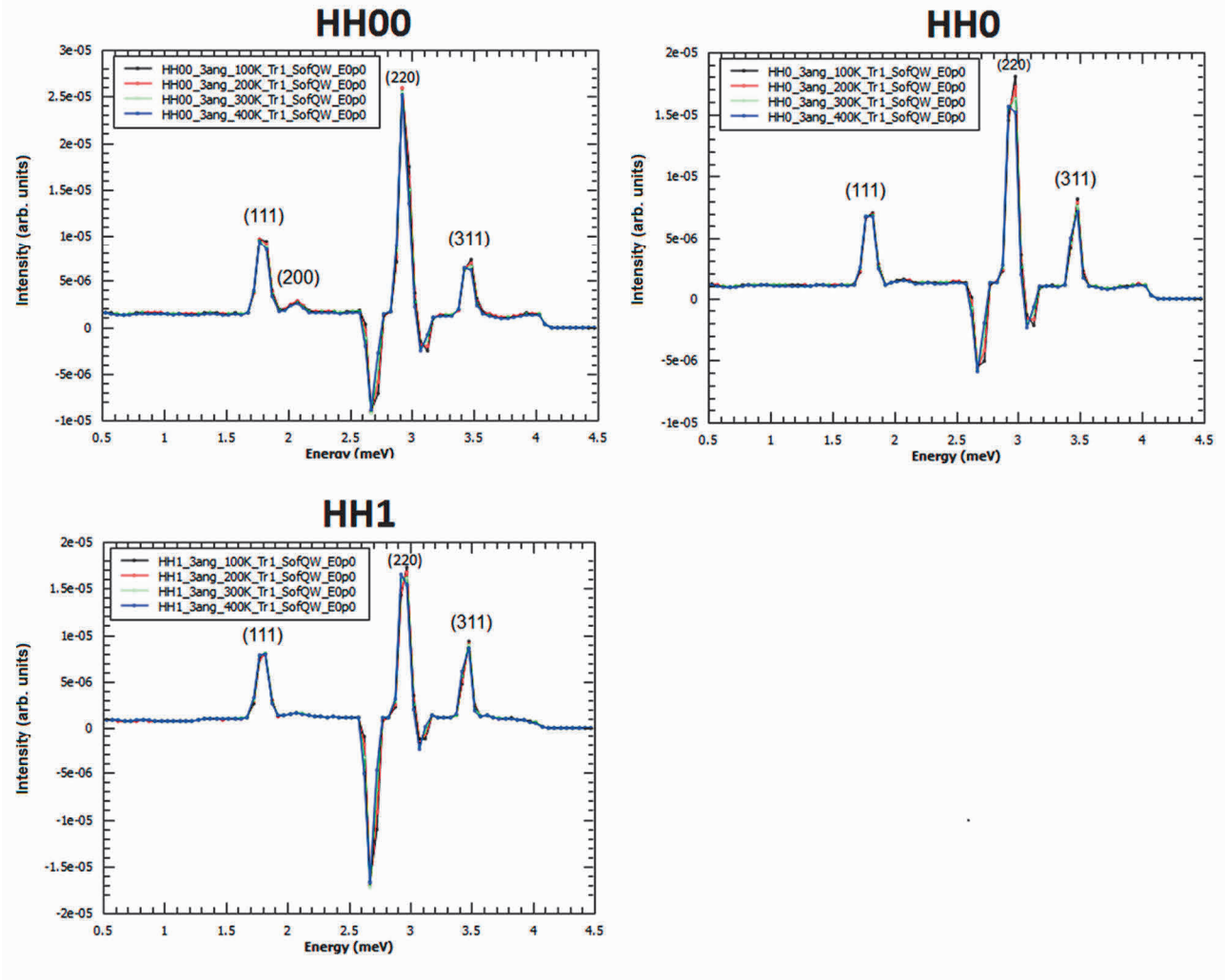

Figure 1 Elastic part of the neutron spectrum of HH samples

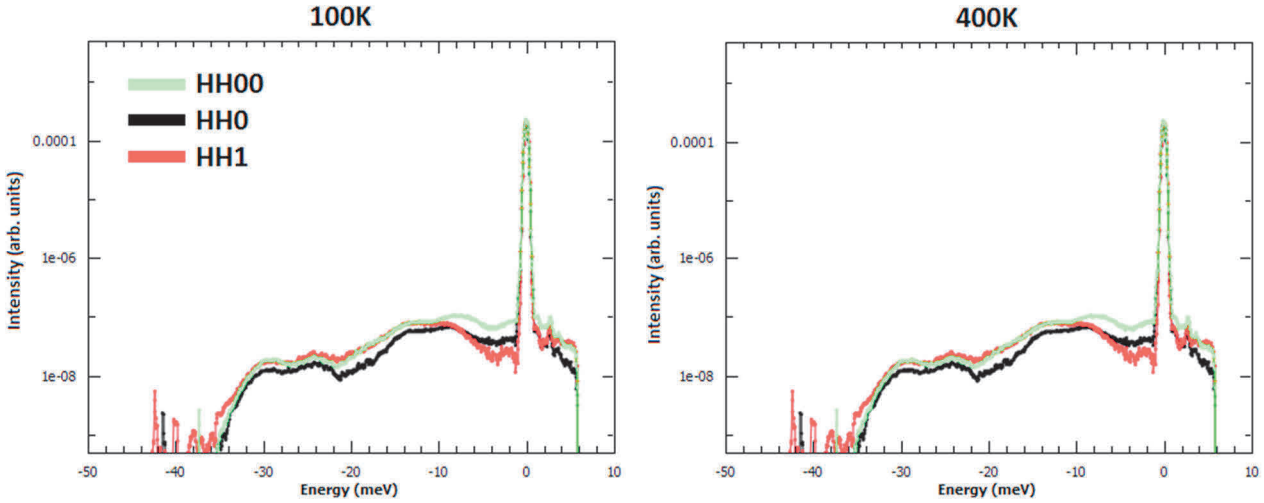

Figure 2 Comparison of inelastic neutron spectra for 3 HH samples at the same temperatures

More information about the nanostructuring effect we obtain from inelastic part of spectra - phonon DOS. **Figure 2** compares HH samples, normalized to the weight of HH0, at the same temperatures. At each temperature is visible that the well annealed and relaxed HH00 sample exhibits higher intensity than

HH0 sample after ball milling and spark plasma sintering. Therefore, we can say that nanostructuring effectively suppresses phonons, since both samples have the same chemical composition, and they differ just in the method of preparation. **Figure 2** shows phonon DOS only at 100 K and 400 K. The graphs for 200 K and 300 K looks very similar. Overall intensity loss caused by nanostructuring is more visible on $S(Q,\omega)$ plots of samples HH00 and HH0 measured at 400 K, see **Figure 3**.

Sample HH1 cannot be directly compared to the origin HH00 sample because of the addition of β-$FeSi_2$, which has different scattering length than pure HH alloy. However, the effect of doping with dispersion phase β-$FeSi_2$ is clearly visible in region from 0 to -10 meV, where sample HH1 has lower intensity then HH0 and so we can say that doping is effectively suppressing phonons at lower frequencies.

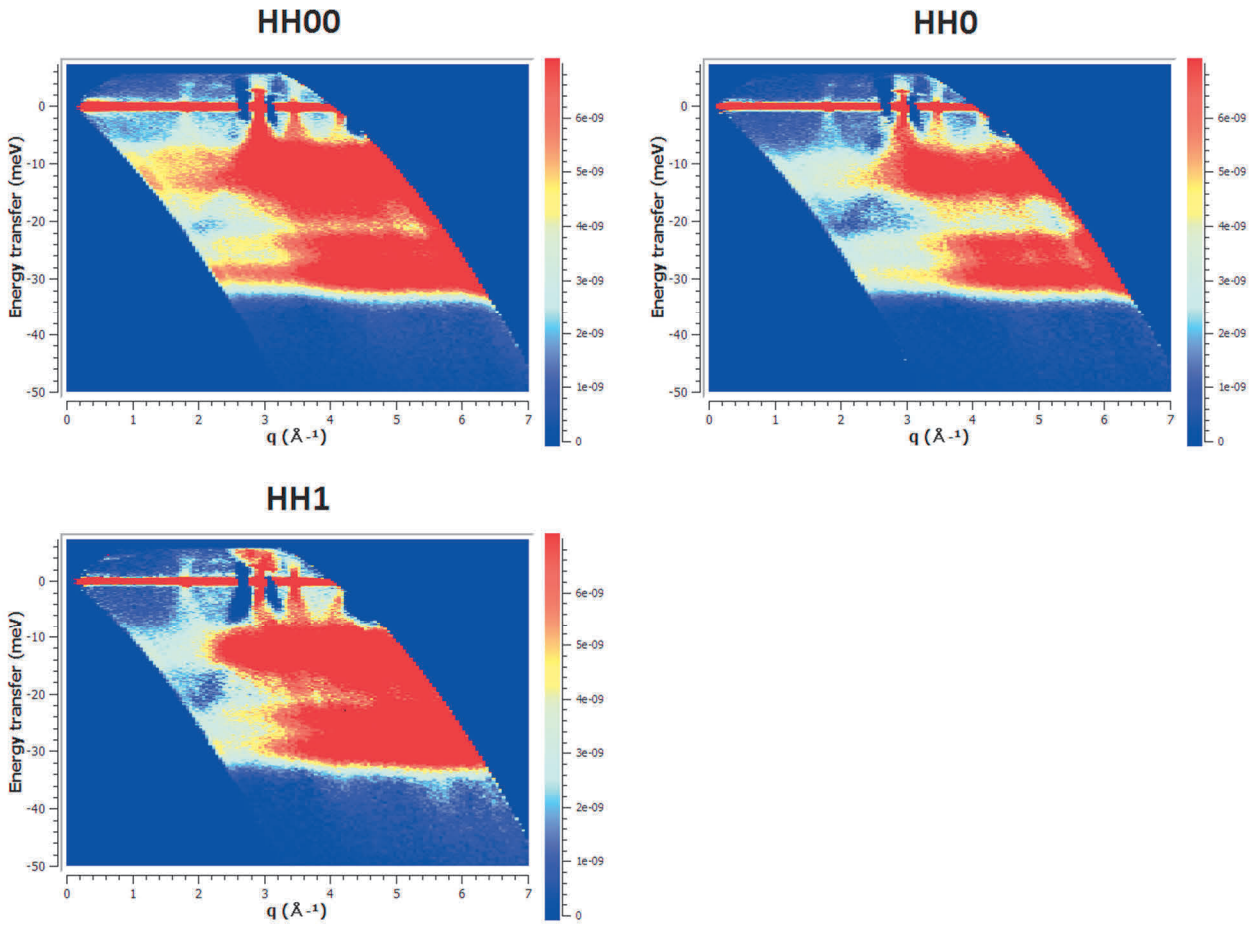

Figure 3 $S(Q,\omega)$ plots of INS for HH samples measured at 400 K normalized to weight of HH0 sample

6. CONCLUSION

In here presented study, effects of high energy ball milling and doping with dispersion β-$FeSi_2$ phase on half-Heusler thermoelectric alloys was investigated by means of inelastic neutron scattering experiments. The following results were obtained. Elastic part of INS spectra documents effective suppression of (200) Bragg peak caused by ball milling. Inelastic signals of the ball milled HH0 sample shows overall intensity decrease compared to relaxed alloy HH00 in wide temperature range. The $S(Q,\omega)$ plots from the nanostructured samples show significantly lower intensity what confirm effective phonon suppression. The dispersion β-$FeSi_2$ inclusion effect is most pronounced in the lower frequencies below - 10 meV, where the HH1 sample shows further phonon suppression. These phonon suppression effects are in agreement with our thermal conductivity

measurements of HH samples where sample HH1 shows significantly lower thermal conductivity than sample HH0.

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