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# Thermoelectric Properties of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_2Te$ Multi-Layered Structures

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## ABSTRACT

Thermoelectric properties of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures with period of 5 nm were studied in temperature ranging from 300 K to 500 K. Structures were prepared by Pulsed Laser Deposition (PLD) on fused silica quartz glass substrates at the substrate temperature during the deposition Ts = 230˚C and Ts = 250˚C with the laser beam energy density Ds = 3 $Jcm^{-2}$. In the contribution temperature dependencies of the in-plane electrical conductivity, the Seebeck coefficient and the resultant power factor together with room temperature value of thermoelectric figure of merit are presented.

**Keywords:** Thermoelectrics; PLD Deposition; Thin Layers; Multi-Layered Systems

## 1. Introduction

Skutterudites have been of high interest as a promising candidate for thermoelectric applications. The key advantage of skutterudites is their possible high figure of merit ZT [1-3]. ZT is the essential material property for thermoelectric energy conversion. It is proportional to the electrical conductivity, temperature and to the square of the Seebeck coefficient and it is disproportional to the thermal conductivity of a material.

The lattice thermal conductivity can be reduced by substituting Co with Fe as in our case.

A great improvement of thermoelectric properties was mathematically and also experimentally proved by preparing materials in the form of a low dimensional system [4-13] such as thin layer, superlattice or multi-layered structure. Such improvement in comparison with bulk materials was published for the skutterudite superlattices [14].

Earlier we published results on thin skutterudite layers prepared by PLD in Ar atmosphere from the $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ hot pressed target [15]. The best thermoelectric properties were obtained on the layers prepared at Ts = 250˚C. All layers were of P-type electrical conductivity [15].

Recently, we prepared thin skutterudite layers by PLD in Ar atmosphere from the $FeSb_2Te$ hot pressed target. The best thermoelectric properties were obtained on the layers prepared at Ts = 250˚C and Ts = 230˚C with Ds = 3 $Jcm^{-2}$. Such layers were also of P-type electrical conductivity. Bulk ternary skutterudite $FeSb_2Te$ had been examined and published in details before [16,17] and was proved to be a good thermoelectric material.

In this contribution, we examine thin thermoelectric multi-layered $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ system composed of thin equidistant layers $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}$ and $FeSb_{2.1}Te$ each 5 nm in thickness (5 nm period) prepared by PLD on a fused silica quartz glass substrate. The structures were prepared at Ts = 230˚C and Ts = 250˚C with Ds = 3 $Jcm^{-2}$. It is expected that the preparation of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structure can be successful because of the similar lattice constant of both materials [16-18] and that an improvement of thermoelectric properties in comparison to the thin single layers might be achieved.

## 2. Methods

PLD targets of $FeSb_2Te$ and $Ce_{0.1}Fe_{0.7}Co_{3.3}Sb_{12}$ composition where synthesized from individual elements by high-temperature solid-state reactions. Stoichiometric amounts of Fe (99.9%), Sb (99.999%), Te (99.999%) and Ce (99.9%), Fe (99.9%), Co (99.9%) and Sb (99.999%) were sealed into evacuated carbon-coated silica glass tubes and heated up to 1050˚C for 48 hrs in a furnace. After quenching into a water bath, the same ampoule was placed into the furnace and annealed at 550˚C for 120 hrs. The resultant material was then ground under acetone, pelletized and heated again at 550˚C for 120 hrs. The completion of the solid-state reaction of obtained powder samples was verified by powder XRD.

The final targets for PLD deposition 20 mm in diameter and 2 mm in height were prepared by the hot pressing method (temperature 500˚C, pressure ~60 MPa for 1 hr). The measured density of pressed targets was found about 96% - 98% of theoretical density.

The basic schema of the experimental apparatus for PLD is depicted in **Figure 1**. Conceptually and experimentally, PLD is an extremely simple method, probably the simplest of all thin film growth techniques. A high power pulsed excimer KrF laser (COMPexProTM 205 F) radiation (1) is used as an external energy source to vaporize materials of target (5) and to deposit a thin film. A set of optical components is used to focus the laser beam to the target surface (2, 3). After the laser pulse irradiation the temperature rises very rapidly (1011 $Ks^{-1}$) and the evaporation becomes non-equilibristic. In our experiment substrates were cleaned from the mechanical dirt in an ultrasonic cleaner. After that the substrates were subsequently cleaned in acetone, toluene and in ethanol. Cleaning in the vapours of boiling ethanol then completed this process. Fused silica substrates were finally annealed in an oven at a temperature around 250˚C. The layers and multi-layered structures were deposited on fused silica quartz glass substrate 10 × 10 mm. The deposition took place at Ar atmosphere (13 Pa). The distance of the substrate from the target was set to 40 mm.

The $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures composed of thin equidistant $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}$ and $FeSb_{2.1}Te$ layers of 5 nm in thickness and total thickness of about 60 nm were prepared by PLD at Ts = 230˚C and Ts = 250˚C with Ds = 3 $Jcm^{-2}$. The deposition conditions were chosen based on previous results taken on single $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}$ [15] and $FeSb_{2.1}Te$ layers as the conditions giving the best thermoelectric properties.

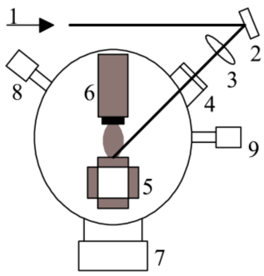

**Figure 1. The basic scheme of the experimental apparatus for PLD: (1) laser beam, (2) mirrors, (3) focusing lens, (4) quartz window, (5) target holder, (6) substrate holder, (7) vacuum pump, (8, 9) Pirani and Penning vacuum gauges, respectively.**

Transport properties, such as the in-plain electrical resistivity and the Seebeck coefficient, were measured on each multi-layered structure and on single layers in the temperature range from 300 K up to 500 K. The power factor was then calculated. Four square shaped contacts for the measurements were prepared by evaporating Ti. Pressed Pt/PtRh thermocouples with diameter of 0.07 mm were used as leads. A conventional DC van der Pauw's method was used for the electrical conductivity measurement. The experimental error of this method is about 10% for the conductivity measurement.

The Seebeck coefficient was determined from the variation of the electromotive force for different temperature gradients across the layer. The both sides of the sample were in the thermal contact with an independent wire resistant sub-heater that supplies the heat and induces the sample temperature gradient. The thermocouple junctions were bonded to each corner of the square shaped sample. The experimental error of the Seebeck coefficient measurement is about 20%.

## 3. Results and Discussion

The multi-layered $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ structures were prepared by PLD at Ts = 250˚C and Ts = 230˚C with Ds = 3 $Jcm^{-2}$.

The in-plain temperature dependencies of the electrical resistivity of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures are given in **Figure 2**. Both multi-layered structures showed semi-conducting P-type behavior—the decrease of electrical resistivity with the increase of temperature. The measured electrical resistivity of multi-layered structures was lower than the earlier published values obtained on single thin layers of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}$ [15] and $FeSb_{2.1}Te$ in the whole studied temperature range.

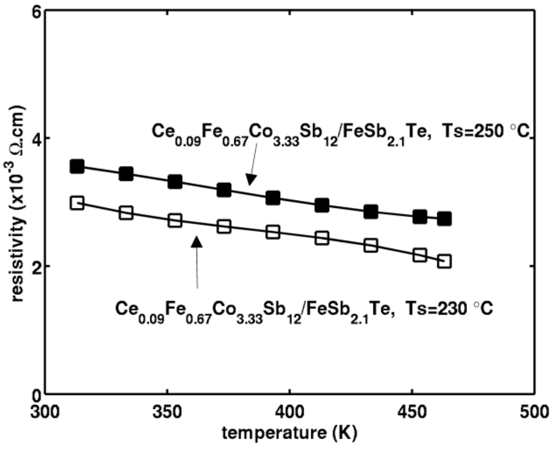

**Figure 2. Temperature dependency of electrical resistivity for $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures prepared at Ts = 230˚C (empty squares) and at Ts = 250˚C (black filled squares).**

The temperature dependencies of the Seebeck coefficient of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures are presented in **Figure 3**. The multi-layered structures showed much lower in-plain Seebeck coefficient in the whole measured temperature range than the previously presented results on single layers [15]. Due to the low Seebeck coefficient, the resultant power factor of all prepared multi-layered structures is lower than the power factor of the best prepared single layers. The in-plain temperature dependencies of the power factor of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures are depicted in **Figure 4**.

If we compare the measured values of power factor of the $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures with published bulk $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ material [1], we found that multi-layered system values are quite worse—roughly four times lower at room temperature and roughly ten times lower at about 500 K. If the decrease of thermal conductivity on multi-layered structure in comparison to bulk material is taken into account, we may speculate that even better values of ZT for prepared multi-layered systems may be achieved in comparison with the bulk $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ material. It is assumed that cross-sectional electrical conductivity and Seebeck coefficient are not much influenced by interfaces in the multi-layered structures. Temperature dependency of power factor of bulk $FeSb_2Te$ has never been published, so the power factor of multiple-structures can not be compared.

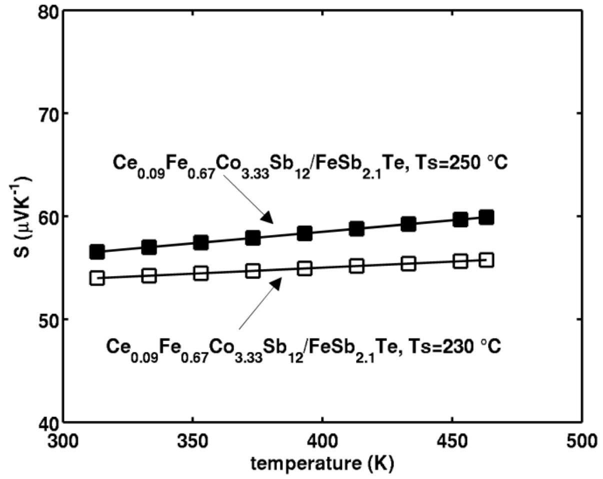

**Figure 3. Temperature dependency of Seebeck coefficient for $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures prepared at Ts = 230˚C (empty squares) and at Ts = 250˚C (black filled squares).**

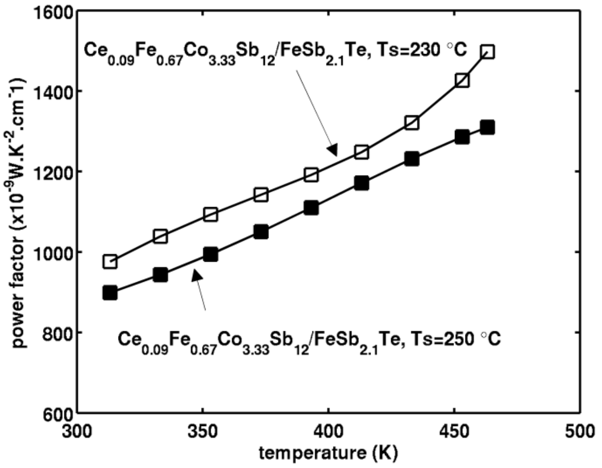

**Figure 4. Temperature dependency of the power factor for $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ multi-layered structures prepared at Ts = 230˚C (empty squares) and at Ts = 250˚C (black filled squares).**

The room temperature value of ZT of the two multi-layered $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ structures (60 nm and 124 nm in thickness) with period 2 nm prepared at Ts = 230˚C with Ds = 3 $Jcm^{-2}$ were measured by Harman method. We found ZT ~ 0.12 for thinner multi-layered structure (60 nm in thickness). This value is more than two times larger than room temperature ZT ~ 0.05 published for bulk $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [1] and much larger than the room temperature ZT ~ 0.024 published for the bulk $FeSb_2Te$ [16,17]. The room temperature ZT ~ 0.25 measured on thicker structure (124 nm in thickness) is about two times bigger. It means that the improvement of ZT in our case depends mainly on the number of the interfaces in multi-layered structure.

## 4. Conclusions

Multi-layered $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}/FeSb_{2.1}Te$ structures composed of equidistant 5 nm $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}$ and $FeSb_{2.1}Te$ layers were successfully prepared by PLD at Ts = 250˚C and Ts = 230˚C with Ds = 3 $Jcm^{-2}$. The measured thermoelectric properties were worse than previously published results on the single thin layers. But to make an overall evaluation of thermoelectric properties, the Harman measurement of thermoelectric figure merit and a measurement of the thermal conductivity, which is expected to decrease due to number of interfaces in the structure, are necessary.

The room temperature ZT of multi-layered structures with period of 2 nm measured by Harman method are promising (ZT ~ 0.12 and ZT ~ 0.25 for 60 nm and 124 nm thick multi-layered structures, respectively) and exceed ZT of both bulk materials. The further ZT improvement is expected by using flatter layers, optimization of deposition conditions and using $Ce_{0.29}Fe_{1.5}Co_{2.5}Sb_{12}$ material instead of $Ce_{0.09}Fe_{0.67}Co_{3.33}Sb_{12}$.

## 5. Acknowledgements

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