Properties of thermoelectric Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te multi-layered structures prepared by laser ablation

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Abstract. Multi-layered Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te structures composed of thin equidistant layers were prepared by Pulsed Laser Deposition on fused silica quartz glass substrates. The structures were prepared at different substrate temperatures (230 °C or 250 °C) applying the laser beam energy density of 3 Jcm$^{-2}$. In the contribution we present some thermoelectric properties such as the in-plane electrical conductivity, the Seebeck coefficient and the power factor for the multi-layered structures in the temperature range from 300 K to 500 K. Comparison of multi-layered structure’s thermoelectric properties with single thin Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ and FeSb$_{2.1}$Te layers is given. A cross sectional picture of the multi-layered structure made by Scanning Electron Microscope is presented for the thicker multi-layered structure.

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 (ZT=0.8 at T=750 K for bulk Ce$_{0.12}$Fe$_{0.71}$Co$_{3.29}$Sb$_{12}$ $^1$, ZT=1.1 at T=750 K for bulk Ce$_{0.28}$Fe$_{1.5}$Co$_{2.5}$Sb$_{12}$ $^2$ and Ce$_{0.9}$Fe$_{3}$CoSb$_{12}$ $^3$. Theoretical maximum ZT=1.4 at 1000 K was predicted for Ce$_{0.9}$Fe$_{3}$CoSb$_{12}$ $^3$. ZT is the essential material property for thermoelectric energy conversion on the Earth and in the cosmos. The dimensionless figure of merit is expressed by a formula:

$$ZT = \frac{S^2 \sigma T}{\lambda}$$

(1)

where S, $\sigma$, T and $\lambda$ are the Seebeck coefficient, the electrical conductivity, the ambient temperature and the thermal conductivity, respectively. The term $S^2\sigma$ is called power factor and can be used for evaluation of thermoelectric material if thermal conductivity $\lambda$ is unknown.

The simplest skutterudites crystallize in a body-centered-cubic structure of the spare group Im3. The low thermal conductivity of skutterudites is obtained by filling the voids in the structure with
small diameter, large-mass interstitials such as for example Yb, Ce or Ba. The lattice thermal conductivity can be also 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, which can be prepared by simultaneous deposition of very thin layers of two or more different materials. Such improvement in comparison with bulk materials was published for the thin skutterudite layers of CoSb$_3$ [14,15] or for the skutterudite superlattices [16].

There have been just a few methods for a thin skutterudite layer or a superlattice deposition published in literature up to date. These are magnetron rf-sputtering [8,15,17], DC magnetron sputtering [18-20], ion-beam sputtering [21], electrochemical deposition [22], simultaneous vaporization of elements which are components of skutterudite followed by temperature treatment in ambient or vacuum [23-26] and Pulsed Laser Deposition (PLD) from a skutterudite target [14,16,23,27-44].

Earlier we published results on thin skutterudite layers prepared by PLD in Ar atmosphere from the Ce$_{0.1}$Fe$_{0.7}$Co$_{0.3}$Sb$_{12}$ hot pressed target [29]. The layers were well crystalline when deposited with the laser beam density $D_s$=3 Jcm$^{-2}$ at substrate temperature $T_S$ in the range from 200 °C to 250 °C. The best thermoelectric properties were obtained on the layers prepared at $T_S$=250 °C, although intensities of the skutterudite lines in X-ray diffraction analysis (XRD) diffractogram were more intensive for layers prepared at $T_S$=200 °C. All layers were of P-type electrical conductivity [29]. The Wavelength Dispersive analysis (WDX) proved Ce$_{0.09}$Fe$_{0.67}$Co$_{0.33}$Sb$_{12}$ stoichiometry.

Recently, we prepared thin skutterudite layers by PLD in Ar atmosphere from the FeSb$_2$Te hot pressed target. The best thermoelectric properties were obtained on the layers prepared at $T_S$=250 °C and $T_S$=230 °C with $D_s$=3 Jcm$^{-2}$. Such layers were well crystalline and were also of P-type electrical conductivity. The WDX shoved FeSb$_{2.1}$Te layers stoichiometry. Bulk ternary skutterudite FeSb$_2$Te had been examined and published in details before [45,46] 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$_{0.33}$Sb$_{12}$/FeSb$_{2.1}$Te system composed of thin equidistant layers Ce$_{0.09}$Fe$_{0.67}$Co$_{0.33}$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 $T_S$=230 °C and $T_S$=250 °C with $D_s$=3 Jcm$^{-2}$. A comparison of multi-layered structure’s thermoelectric properties with properties of single thin Ce$_{0.09}$Fe$_{0.67}$Co$_{0.33}$Sb$_{12}$ and FeSb$_{2.1}$Te layers are also given. It is expected that the preparation of Ce$_{0.09}$Fe$_{0.67}$Co$_{0.33}$Sb$_{12}$/FeSb$_{2.1}$Te multi-layered structure can be successful because of the similar lattice constant of both materials [45-47].

2. Experimental details

PLD targets of FeSb$_2$Te and Ce$_{0.1}$Fe$_{0.7}$Co$_{0.3}$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 powder X-ray diffraction patterns of FeSb$_2$Te ternary compounds used for the target were collected in the Bragg-Brentano geometry on a Bruker D8 Advance diffractometer. CuKα radiation was used. The crystal structure of FeSb$_2$Te was refined by the Rietveld method for X-ray powder
diffraction data using the FullProf program [23]. XRD spectrogram of target compound is depicted in figure 5 (top view).

![Figure 1](image_url)

**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.

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 10x10 mm. The deposition took place at Ar atmosphere (13 Pa). The distance of the substrate from the target was set to 40 mm.

Series of multi-layered \(\text{Ce}_{0.09}\text{Fe}_{0.67}\text{Co}_{3.33}\text{Sb}_{12}/\text{FeSb}_{2.1}\text{Te}\) structures composed of thin equidistant \(\text{Ce}_{0.09}\text{Fe}_{0.67}\text{Co}_{3.33}\text{Sb}_{12}\) and \(\text{FeSb}_{2.1}\text{Te}\) layers of 5 nm in thickness and total thickness of about 60 nm were prepared by PLD at \(T_s=230\) °C and \(T_s=250\) °C with \(D_s=3\) Jcm\(^{-2}\). The deposition conditions were chosen based on previous results taken on single \(\text{Ce}_{0.09}\text{Fe}_{0.67}\text{Co}_{3.33}\text{Sb}_{12}\) and \(\text{FeSb}_{2.1}\text{Te}\) layers as the conditions giving the best thermoelectric properties.

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 %.

The thickness of the layers was measured using a mechanical stylus profile-meter (\(\alpha\)-Step 500, Tencor Instruments, U.S.A). The uncertainty in the thickness estimation is about 10 % in the examined range of thicknesses partly because of the fact that the layer thickness in the centre of the sample is higher than on its edge.

Scanning Electron Microscope (SEM) images were measured using Leo 1550 device (magnification up to 500 k). To see the edge of the layer, the sample was scanned under 45°.

3. Results and discussion

3.1. Single thin layers
The best single layer prepared from $\text{Ce}_{0.1}\text{Fe}_{0.7}\text{Co}_{3.3}\text{Sb}_{12}$ target was prepared at $T_s=250 \, ^\circ C$ with $D_s=3 \, \text{Jcm}^{-2}$. It showed semi-conducting P-type temperature behaviour of the electrical resistivity. The measured value was roughly 8.5 times higher at room temperature and roughly 5 times higher at 500K in comparison with published bulk $\text{Ce}_{0.12}\text{Fe}_{0.71}\text{Co}_{3.29}\text{Sb}_{12}$ data [1]. The room temperature value of measured Seebeck coefficient of the layer was roughly 1.4 times higher in comparison with bulk $\text{Ce}_{0.12}\text{Fe}_{0.71}\text{Co}_{3.29}\text{Sb}_{12}$ [1] but we observed lower temperature slope, so the measured value is comparable with the published bulk material value at 500K [1]. Temperature dependencies of electrical resistivity and Seebeck coefficient are depicted in figure 2.

Figure 2. Temperature dependencies of the electrical resistivity (squares) and the Seebeck coefficient (triangles) for the 64nm thick P-type layer prepared from $\text{Ce}_{0.1}\text{Fe}_{0.7}\text{Co}_{3.3}\text{Sb}_{12}$ target at $T_s=250 \, ^\circ C$ with $D_s=3 \, \text{Jcm}^{-2}$.

The WDX composition study done on 439 nm thick single layer proved an average stoichiometry of $\text{Ce}_{0.09}\text{Fe}_{0.67}\text{Co}_{3.33}\text{Sb}_{12}$. The maximal deviation was in both cases less than +/-3 % for all elements.

The XRD measurement done on 439 nm thick single layer proved that the layer was well crystalline with CoSb$_3$ structure.

The temperature dependencies of the electrical resistivity and the Seebeck coefficient for single thin layers prepared from FeSb$_2$Te target at $T_s=230 \, ^\circ C$ and $T_s=250 \, ^\circ C$ with $D_s=3 \, \text{Jcm}^{-2}$ are depicted in figure 3.

Figure 3. Temperature dependencies of the electrical resistivity (squares) and the Seebeck coefficient (triangles) for the 65 nm thick P-type layer prepared from FeSb$_2$Te target at $T_s=230 \, ^\circ C$ and 62 nm $T_s=250 \, ^\circ C$ with $D_s=3 \, \text{Jcm}^{-2}$.

Both layers showed semi-conducting P-type behaviour of the electrical resistivity (the electrical resistivity decreases with rising temperature). The room temperature values of electrical resistivity of the layers were higher than the value published for bulk FeSb$_2$Te material ($1.59\times10^{-3} \, \text{Ohmcm at 25 } ^\circ C$) [20] and also higher than value measured on PLD target ($2.50\times10^{-3} \, \text{Ohmcm at 25 } ^\circ C$), see table 1.
Table 1 The comparison of the room temperature values of the electrical resistivity, the Seebeck coefficient and the power factor of PLD layers prepared at $T_s=230 \, ^\circ C$ with $D_s=3 \, J/cm^2$ and $T_s=250 \, ^\circ C$ with $D_s=3 \, J/cm^2$ from FeSb$_2$Te target with bulk FeSb$_2$Te material [45] and used PLD target.

| Temp 25°C | Bulk FeSb$_2$Te [20] | PLD FeSb$_2$Te target | FeSb$_2$Te layer, $T_s=250 \, ^\circ C$ | FeSb$_2$Te layer, $T_s=230 \, ^\circ C$ |
|-----------|---------------------|----------------------|-------------------------------------|-------------------------------------|
| $R$ (m$\Omega$cm) | 1.59                | 2.50                 | 5.08                                | 7.02                                |
| $S$ ($\mu$V/K)   | 54.70               | 112.96               | 119.00                              | 104.57                              |
| $S^2/R \times 10^9$ (WK$^{-2}$ cm$^{-1}$) | 1881.82             | 5140.63              | 2786.87                             | 1557.45                             |

The room temperature values of Seebeck coefficient of FeSb$_2$Te single layers prepared at $T_s=230 \, ^\circ C$ with $D_s=3 \, J/cm^2$ and $T_s=250 \, ^\circ C$ with $D_s=3 \, J/cm^2$ are about twice higher than published values for bulk FeSb$_2$Te material [45]. Prepared layers showed higher Seebeck coefficients in the whole studied temperature range from room temperature up to 500 K in comparison with values for bulk FeSb$_2$Te material [46]. The layer prepared at $T_s=230 \, ^\circ C$ with $D_s=3 \, J/cm^2$ had lower room temperature value of power factor 1557.45$\times 10^9$ WK$^{-2}$ cm$^{-1}$ than the value published for bulk material [45, 46] and also than layers prepared at $T_s=250 \, ^\circ C$ with $D_s=3 \, J/cm^2$. But the power factor’s slope for the layer prepared at $T_s=230 \, ^\circ C$ with $D_s=3 \, J/cm^2$ suggests that it may be comparable with layers prepared at $T_s=250 \, ^\circ C$ for higher temperatures (above 500 K).

WDX experiments that were done on the thicker layers proved average FeSb$_{2.1}$Te stoichiometry that corresponds very well to the target composition.

XRD experiments done on the thicker layers with thickness 240 nm and 235 nm prepared at $T_s=230 \, ^\circ C$ and $T_s=250 \, ^\circ C$ with $D_s=3 \, J/cm^2$, respectively, proved that both layers were well crystalline with peaks corresponding to the used PLD target.

The resulting dependency of power factor versus temperature for the best single PLD layers is together with the published bulk Ce$_{0.12}$Fe$_{0.71}$Co$_{3.29}$Sb$_{12}$ data [1] depicted in figure 4. The power factors of our best prepared single layers are much smaller (roughly twice smaller at room temperature and roughly 5 times smaller at 500K) in comparison with the bulk Ce$_{0.12}$Fe$_{0.71}$Co$_{3.29}$Sb$_{12}$ [1]. Temperature dependency of power factor of bulk FeSb$_2$Te has never been published. For the bulk material there was only room temperature value of power factor about 1881.8$\times 10^9$ WK$^{-2}$ cm$^{-1}$ published [45,46].

![Figure 4](image_url)

**Figure 4.** Temperature dependencies of the power factor for the single layers prepared from Ce$_{0.12}$Fe$_{0.71}$Co$_{3.29}$Sb$_{12}$ target at $T_s=250 \, ^\circ C$ with $D_s=3 \, J/cm^2$, thickness 64 nm (triangles) and from FeSb$_2$Te target at $T_s=230 \, ^\circ C$ with $D_s=3 \, J/cm^2$, 65 nm thickness (circles) and $T_s=250 \, ^\circ C$ with $D_s=3 \, J/cm^2$, 62 nm thickness (squares) together with the published data for bulk Ce$_{0.12}$Fe$_{0.71}$Co$_{3.29}$Sb$_{12}$ [1].

3.2. *Multi-layered structures*
The multi-layered Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te structures (about 60 nm in total thickness) composed of thin equidistant Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ and FeSb$_{2.1}$Te layers (5 nm in thickness) were prepared by PLD at $T_s=250$ °C with $D_s=3$ Jcm$^{-2}$ and at $T_s=230$ °C with $D_s=3$ Jcm$^{-2}$ with aim to improve thermoelectric properties of single thin Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ and FeSb$_{2.1}$Te layers prepared before.

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 (60 nm in total thickness) are given in figure 5. Both structures showed semi-conducting P-type behaviour of the electrical resistivity (the decrease of electrical resistivity with the increase of temperature). The multi-layered structures had lower electrical resistivity than the best above mentioned single layers Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ and FeSb$_{2.1}$Te in the whole studied temperature range.

![Figure 5](image-url)

*Figure 5.* Temperature dependency of electrical resistivity for 60 nm thick Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te multi-layered structures prepared with $D_s=3$ Jcm$^{-2}$ at $T_s=230$ °C (empty squares) and at $T_s=250$ °C (black filled squares).

The multi-layered structures showed also much lower in-plain Seebeck coefficient in the whole measured temperature range than the single layers. 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.

When we compared 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 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$_{2}$Te has never been published, so the power factor of multiple-structures can not be compared. Only the room temperature value of power factor of about 1881.8x10$^{-9}$WK$^{-2}$cm$^{-1}$ was published [45,46].
The temperature dependencies of Seebeck coefficient and resultant power factor for 60 nm thick Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te multi-layered structures composed of thin equidistant layers (5 nm in thickness) prepared at Ts=230 °C and 250 °C with Ds=3 Jcm$^{-2}$ are given in figure 6 and Figure 7, respectively.

The SEM study was done on 286 nm thick multi-layered structure composed of altering equidistant layers of Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ (thickness 17.5 nm) and FeSb$_{2.1}$Te (thickness 18.3 nm). The SEM cross sectional picture of multi-layered structure is presented in figure 8, where individual layers were visible.
Figure 8. The SEM cross sectional picture of Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te multi-layered structure (total structure thickness 286 nm) composed of altering equidistant layers of Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ (17.5 nm in thickness) and FeSb$_{2.1}$Te (18.3 nm in thickness).

4. Conclusions
Multi-layered Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$/FeSb$_{2.1}$Te structures composed of thin equidistant Ce$_{0.09}$Fe$_{0.67}$Co$_{3.33}$Sb$_{12}$ and FeSb$_{2.1}$Te layers (5 nm in thickness) were successfully prepared by PLD at Ts=250 °C and Ts=230 °C with Ds=3 Jcm$^{-2}$. The resultant in-plane power factors of multi-layered structures were lower than the power factors of both used materials in a form of single layer. 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, is necessary.

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