Determination of structural properties of thin thermoelectric $CoSb_x$ and $Yb_yCo_4Sb_{12}$ films using x-ray diffraction

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Since energy efficiency is becoming more and more important, the field of thermoelectricity is particularly in the focus of current research activities. Nanostructured materials [1, 2] as well as new material groups have recently been introduced [3, 4]. One of the promising materials for future application is $CoSb_3$ in its skutterudite phase.

$CoSb_3$ is a semiconductor with a band gap smaller than 0.4 eV. Compared to other semiconductors, $CoSb_3$ has a low thermal conductivity, dominated by phonons. The structure of this alloy (bcc, space group Im3) contains big voids, which can be filled with guest ions like Y or Yb. These guest ions can strongly oscillate and thereby are effective in scattering phonons, which yields to a further decrease in thermal conductivity and consequently a higher thermoelectric efficiency [5, 6]. The electronic properties of the material remain largely unchanged by the filling with ions. Therefore, filled $CoSb_3$ can serve as a model system for a phonon glass electron crystal (PGEC), a concept first introduced by Slack [7].

In this project we have investigated thin polycrystalline $CoSb_x$ films with x ranging from 3 to 4 on different substrates and $Yb_yCo_4Sb_{12}$ films with y ranging from 0 to 4 using x-ray diffraction at HASYLAB beamline G3 at a wavelength of 0.154056 nm closely corresponding to Cu K_α. All films were deposited at room temperature and post-annealed in UHV for 1h.

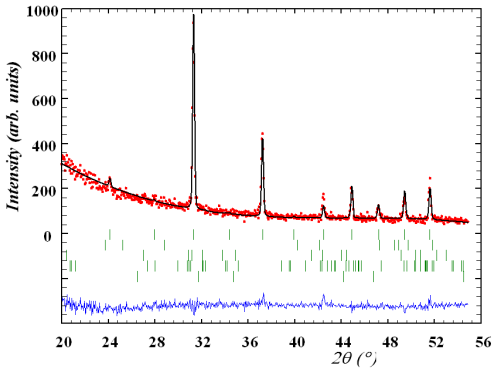
A Rietveld refinement with the program FULLPROF [8] of the patterns of $Yb_yCo_4Sb_{12}$ in the range of $20° < 2\theta < 100°$ confirms the correct position of the filled atoms and allows the determination of the filling fraction. Additionally a series of stress measurements with the $\sin^2(\psi)$ – method were performed for the $CoSb_x$ films, to investigate the dependence of the stress on different Sb content x, cracks in the surface and different substrates with changing thermal expansion coefficient.

$Yb_yCo_4Sb_{12}$

$Yb_yCo_4Sb_{12}$ were deposited by a co-deposition of Sb (effusion cell), Yb (effusion cell) and Co (e-gun) in a MBE chamber with base pressure of 10^{-10} mbar. The Yb content y of the film was varied between 0 and 3.9. The refinement of the measured patterns shows that the fillers can be introduced on the right position of the host structure. With increasing filling fraction the lattice parameter increases, too. The expected linear dependence is not found, which could be explained due to additional peak shifts by film stress, which was not yet included in the analysis. The filling fraction y of Yb determined by refinement for films annealed at 300°C and 500°C and the calculated filling fraction determined out of RBS measured film composition is shown in table 1.

For films annealed at 300°C and filling fraction smaller than 0.6, the XRD (rietveld) and the stöchiometric (RBS) fraction is equal with respect of the errors. Remarkable is the high filling fraction of around 0.5 in comparison to the equilibrium limit of around 0.12, which can be explained by the non-equilibrium deposition method. After annealing at 500°C of the highly filled films the filling fraction relaxes towards this limit. If the initial filling fraction was smaller than the limit, the amount of Yb stays nearly constant.

For filling fractions higher than 0.5 the results are difficult to explain, yet. The behaviour of these films might be explained with formation of Yb_xO_y phases and the energetic competition between filling and oxide formation. Notably here is the high filling fraction after annealing at 500°C of ~0.6 for films with an initial fraction of 1.1.



annealed at 300°C		annealed at 500°C	
$Yb_yCo_4Sb_{12}$ (RBS) y	$Yb_xCo_4Sb_{12}$ (XRD) y	$Yb_yCo_4Sb_{12}$ (RBS) y	$Yb_xCo_4Sb_{12}$ (XRD) x
0,04	0,04	0.05	0.04
0.09	0,09	0.08	0.05
0.12	0,18	0,14	0.13
0.24	0,27	0.30	0.12
0.53	0,48	0.45	0.13
0.60	0,51	0.67	0.10
1.10	0,68	1.16	0.57
2.30	0,13	2.34	0.09
3.90	0,55	3.79	0.30

Figure 1: left: Refinement of the XRD-pattern of a $Yb_yCo_4Sb_{12}$ film. Right: table with filling fraction y of $Yb_yCo_4Sb_{12}$ films deposited at room temperature and annealed at 300°C/500°C. y was estimated with both Rietveld refinement of the XRD patterns and out of the film stoichiometry measured by RBS

$CoSb_x$

To optimize the film surface and to avoid cracks by annealing $CoSb_3$ films were deposited on substrates with different thermal expansion coefficient α. It could be found that the roughness of the surface shows a minimum and that there are no cracks for if α of film and substrate have the same magnitude. To confirm that the stress of these films is lowered stress measurements were done. All investigated films show an high biaxial stress, already measurable at the peak at $2\theta \sim 59°$. Peaks at higher angle were not usable, because of its low signal to noise ratio. The calculated stress with the elastic constants $E = 160$ GPa and $\nu = 0.193$ are for the usual substrate of 100 nm SiO_2 on Si(100) around 700 kPa. The improved value on a special glass is 100 kPa.

Additionally annealed films with different Sb content were investigated, because former measurements show significant peak shifts. The peak shift can be explained by the results of Rietveld refinement and stress measurements, showing that the shifts are caused by internal stress of the films, stress relaxing by cracks in the surface and incorporation of Sb into the voids.

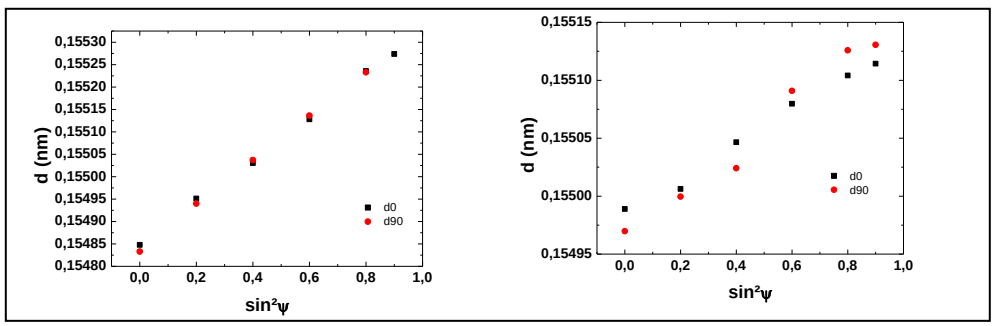


Figure 2: Measured biaxial stress curves of Co_1Sb_3 films on different substrates with the $\sin^2\psi$-method for $\varphi = 0$ and 90°. left: Substrate 100nm SiO_2 on Si (stress 700 kPa); right: special glass (stress 150 kPa)

References

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