Structural, chemical, and thermoelectric properties of Bi_2Te_3 Peltier materials: bulk, thin film, and superlattices

Struktur, chemische Zusammensetzung und physikalische Eigenschaften von Bi_2Te_3 Peltier-Materialien: Volumenmaterialien, Dünnfilme und Übergitterstrukturen

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Correlations structure-chemical composition-thermoelectric properties

Transmission electron microscopy (TEM)

Bi_2Te_3 thin film and $Bi_2Te_3/Bi_2(Te,Se)_3$ superlattice structures

$Bi_2(Te,Se)_3$ and $(Bi,Sb)_2Te_3$ bulk

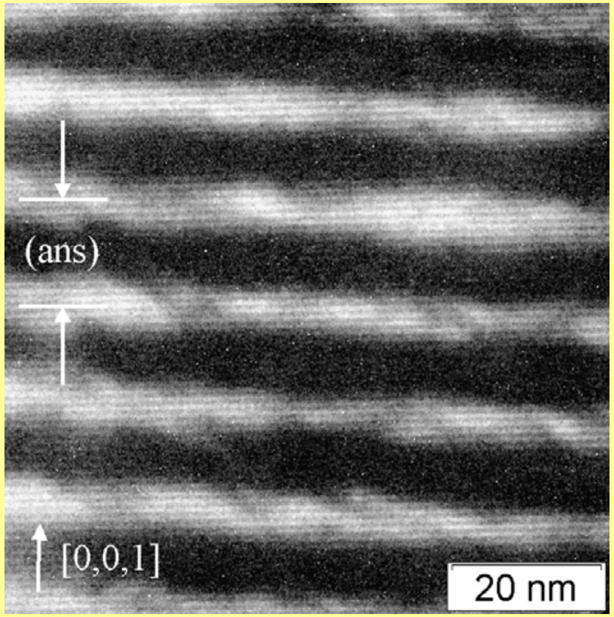
DTG Mitgliederversammlung, November 2009

Thermoelectric properties, structural and chemical modulations (on the nanometer scale)

thermoelectric figure of merit: $ZT = \frac{S^2\sigma}{\lambda_{el} + \lambda_{latt}} T \approx 1$ at 300K

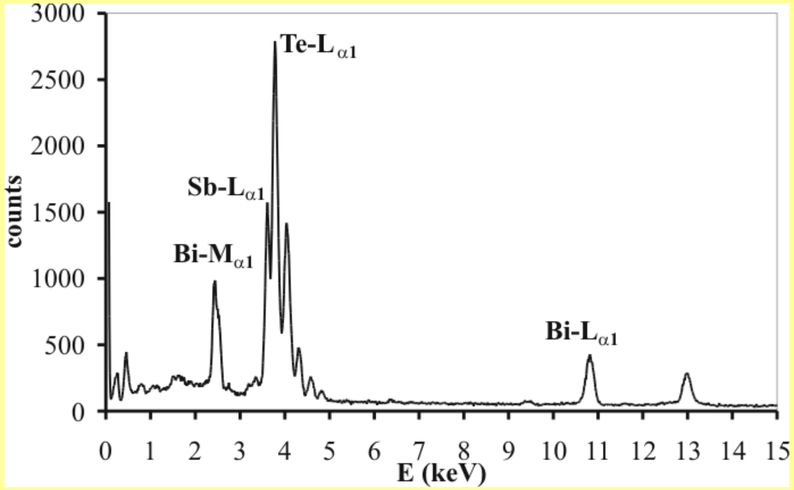
Bi_2Te_3: S ≈ 200 μV/K, σ ≈ 1000 1/Ωcm, **λ ≈ 1 W/mK**

nanostructure



correlation ?

chemical composition



processing of bulk, thin films, superlattices

start	to verify

bulk

start

- chemical composition and extended crystal defects determine transport properties

to verify

- local variations in stoichiometry
- Character and density of extended crystal defects

superlattices

start

- chemical composition
- Epitaxial relations
- superlattice period
- thermoelectric properties

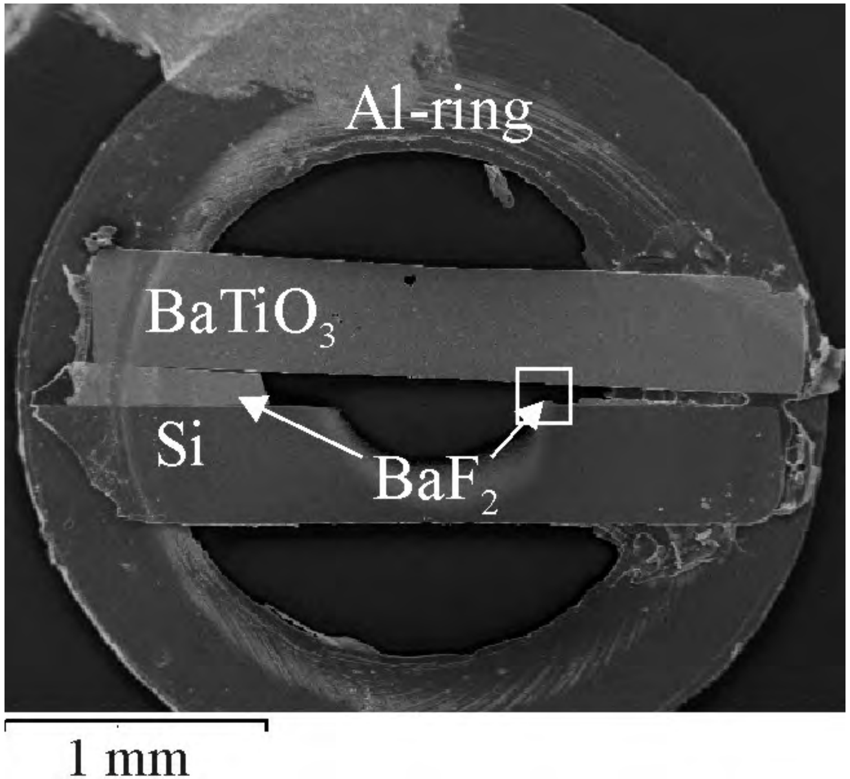
to verify

- Layer and interface roughness
- Extended crystal defects and interaction with superlattices

Transmission electron microscopy

Zeiss912Ω TEM

- 120 keV
- CCD camera, video CCD camera
- double-tilt holder, tilt range 60°/30°
- energy-dispersive X-ray detector (EDX)
- in-column OMEGA energy-filter



Bi_2Te_3: thin films and superlattices

Hicks & Dresselhaus, Phys. Rev. B **47**, 12727 (1993): quantum well with width *a*:

$$ZT \propto \frac{\mu}{\lambda_{\text{latt}}} \frac{1}{a}$$

Venkatasubramanian, Nature **413**, 597 (2001): Bi_2Te_3/Sb_2Te_3 SL, period 6 nm → ***ZT*=2.4**

Fraunhofer IPM:

- Bi_2Te_3 thin films (1µm)
- symmetric $Bi_2Te_3/Bi_2(Te_{0.88}Se_{0.12})_3$ SL, film thickness 1µm, period 6 nm and 12 nm

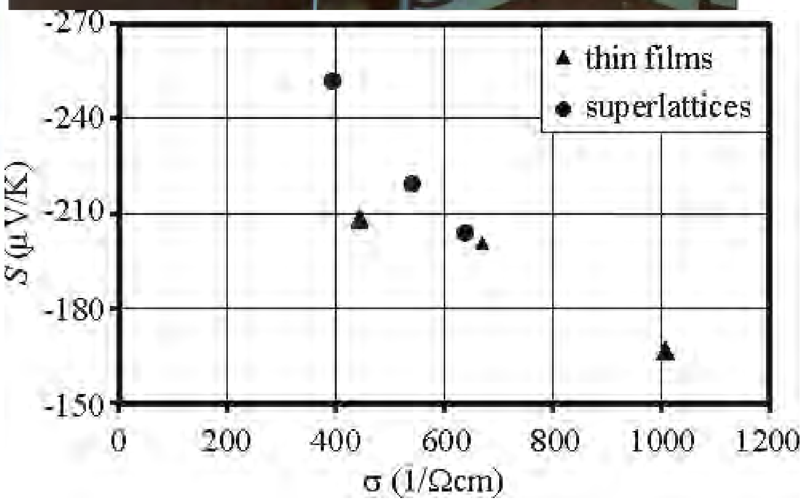
Material	Structure	µ	λ_{latt}	ZT
		cm^2/Vs	(W/mK)	
Bi_2Te_3	bulk	160	1.53	0.46
$Bi_2(Te,Se)_3$	bulk	150	1.15	0.85
Bi_2Te_3	thin film	120	1.60	0.45
$Bi_2Te_3/Bi_2(Te,Se)_3$	SL-12nm		1.07	
$Bi_2Te_3/Bi_2(Te,Se)_3$	SL-10nm	100	1.01	0.60

→ reduction of carrier mobility µ

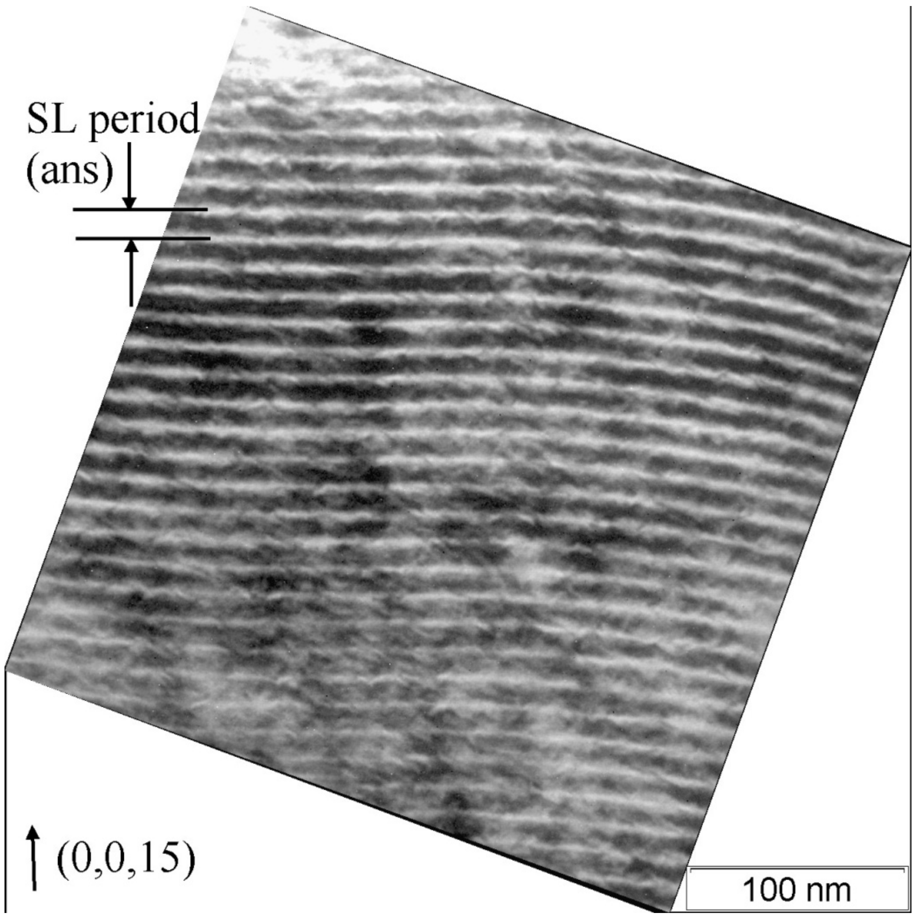
→ reduction of lattice thermal conductivity λ_{latt}

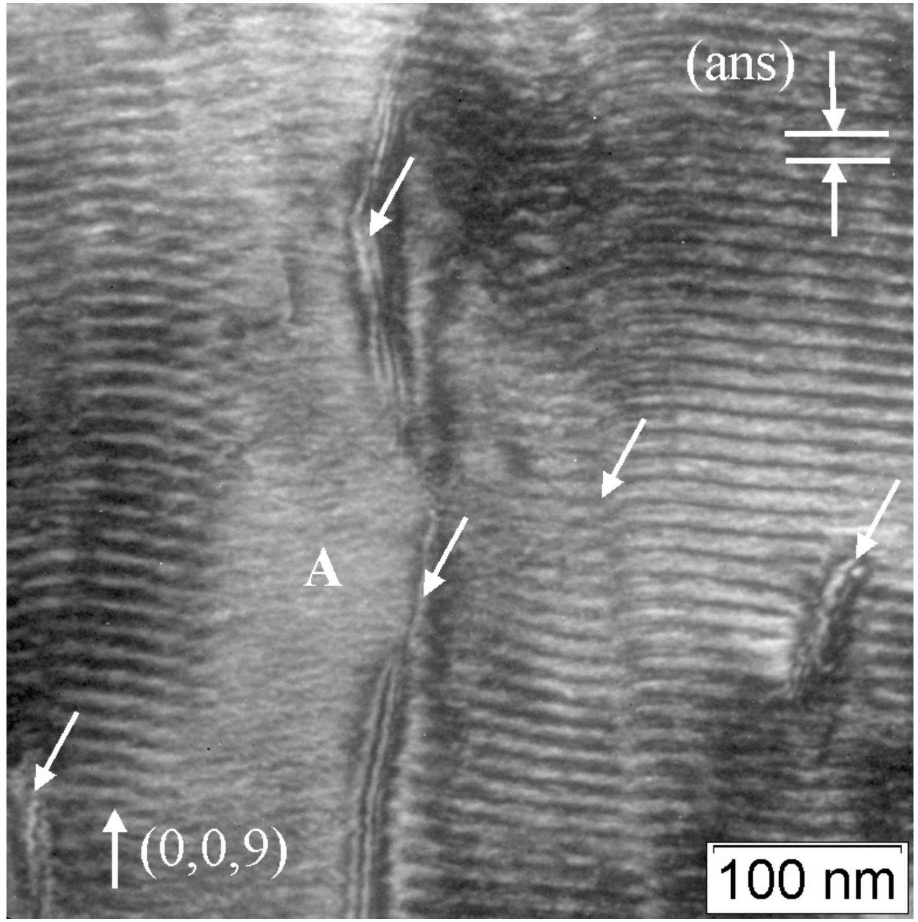
→ no *ZT* enhancement

MBE:(111)-BaF_2 substrate, T_S=290°C; lattice mismatch: 0.05% (in-plane measurements, 300K)



Bi_2Te_3 superlattice (12nm) in cross section



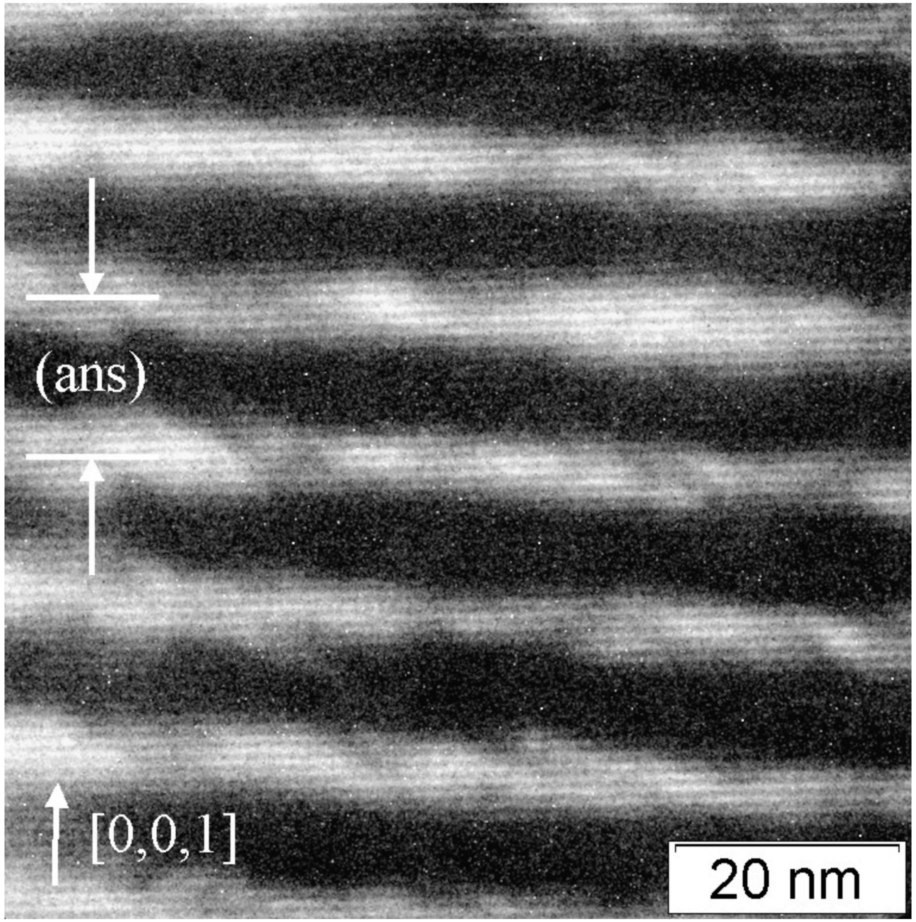


superlattice (ans)
→ period 12.0 nm,
→ slight bending, amplitude 30 nm, wavelength 400 nm

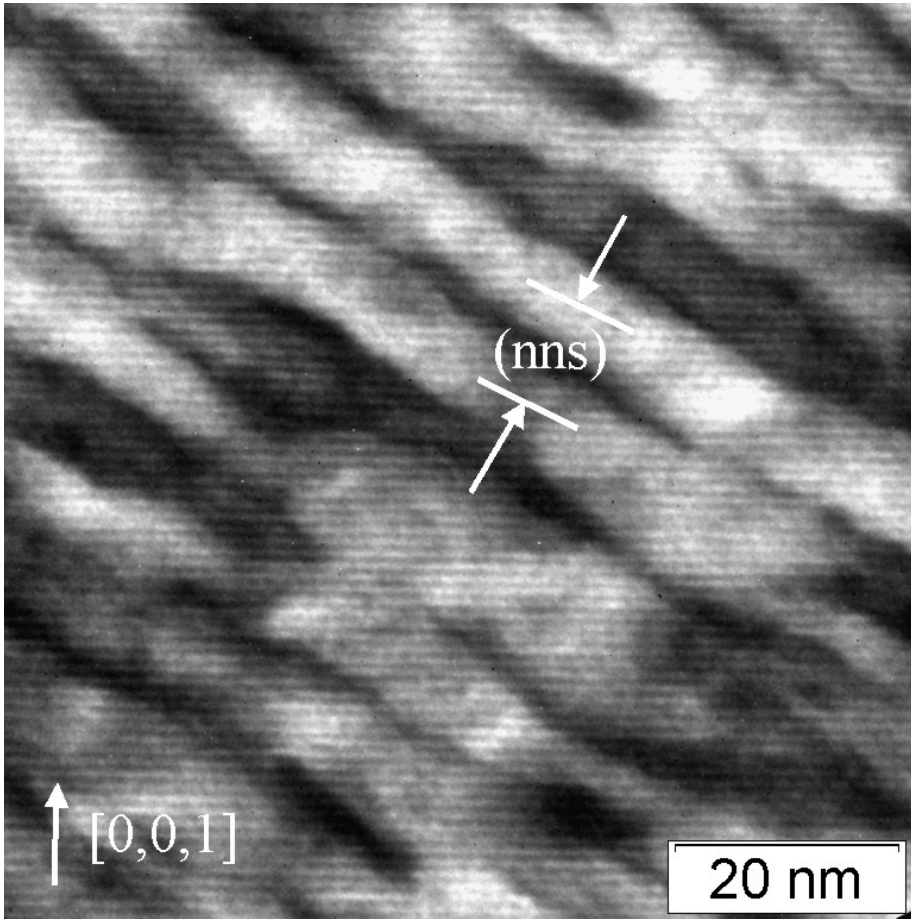
→ threading dislocations with density of $2\times10^{9}cm^{-2}$
→ strong bending of the superlattice
→ SL disappeared in region A

High resolution images of the Bi_2Te_3 superlattice (12nm) in cross section

nns out of contrast



nns in contrast



superlattice (ans)
→ period 12.0 nm
→ no bending of the SL due to nns

structural modulation (nns)
→ wavelength 10 nm and wave vector (1,0,10)
→ no bending of the nns due to SL

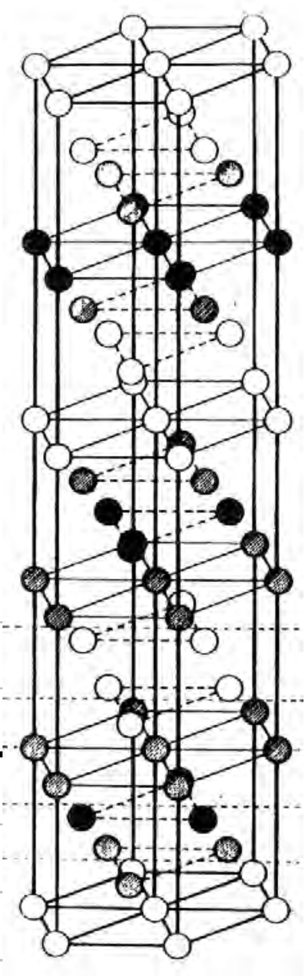
Superlattices, artificial nanostructures (ans)

1. The superlattice structure (ans) can be imaged with strongly excited (0,0,l)-reflections.
2. The SL showed a period of 12.0 nm, bending with an amplitude of 30 nm and a wavelength of 400 nm, and threading dislocations with a density of 2×10^9 cm^{-2}.
3. The lattice thermal conductivity λ_{latt} decreases with decreasing SL period; therefore, superlattices yield an enhanced scattering of phonons.
4. A nns is superimposed to the structure, yielding a significant amount of stress in the samples, which was still not noticed and identified. The stress fields directly affect the transport coefficients, particularly the lattice thermal conductivity.
5. The thermopower and the electrical conductivity were found to be negatively correlated, depend on the charge carrier density, and no clear dependence of the two quantities on the microstructure could be found.

N. Peranio, O. Eibl, and J. Nurnus, „Structural and thermoelectric properties of epitaxially grown Bi_2Te_3 thin films and superlattices“, J. Appl. Phys. 100, 114306 (2006).

Bi_2Te_3 bulk materials

Crystal structure: pseudo-hexagonal (a=0.44 nm, c=3.05 nm)



Peltron samples:

- n-type $Bi_2(Te_{0.91}Se_{0.09})_3$
- p-type $(Bi_{0.26}Sb_{0.74})_{1.98}(Te_{0.99}Se_{0.01})_{3.02}$
- synthesized by the Bridgman technique
- good texture, grain size 5 μm

Thermoelectric properties (300 K, in-plane):

D.M. Rowe, *CRC Handbook of Thermoelectrics*

sample	**n/p**	**μ**	**σ**	**S**	**$S^2\sigma$**	**λ**	**λ_{latt}**	**ZT**
	$10^{19}cm^{-3}$	cm^2/Vs	1/Ωcm	μV/K	$\mu W/cmK^2$	W/mK	W/mK	
Bi_2Te_3	2.00	160	513	227	26	1.73	1.53	0.46
$Bi_2(Te_{0.95},Se_{0.05})_3$	4.00	150	901	-223	45	1.59	1.15	0.85
$(Bi_{0.25},Sb_{0.75})_2Te_3$	3.34	177	781	225	40	1.37	1.07	0.87

→ reduction of lattice thermal conductivity due to **alloy scattering** of the phonons

→ *ZT* enhancement

Knowledge about structure and chemical composition:

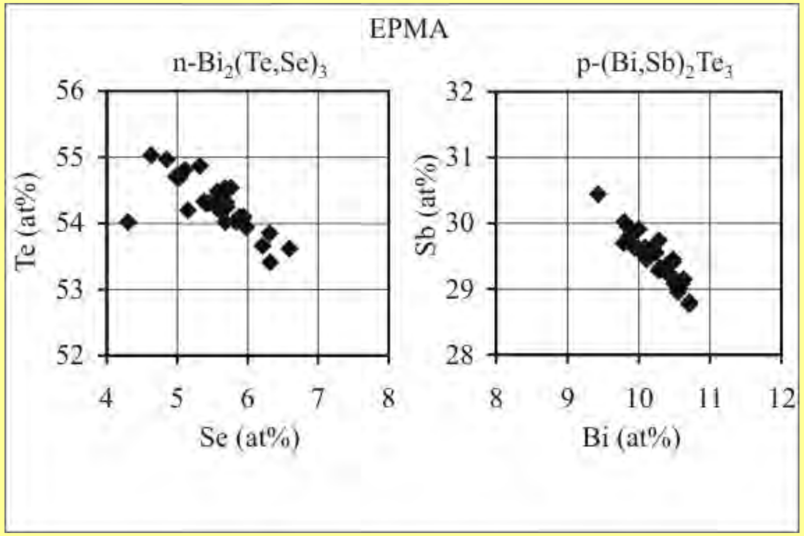
→ Bi_2Te_3 shows a low lattice thermal conductivity λ_{latt} like a highly disordered material

→ no experimental results specified what the structural disorder would be

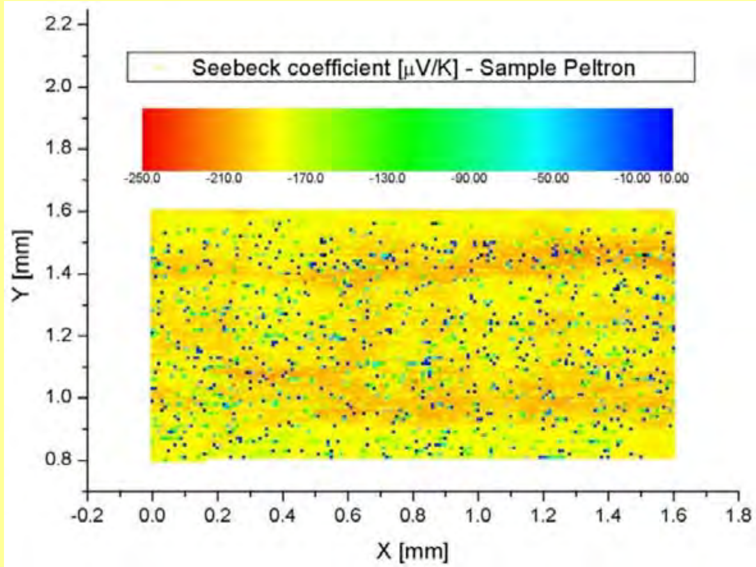
→ Bi_2Te_3 alloys are assumed to be solid solutions

Chemical analysis and Seebeck scanning microprobe (SPM)

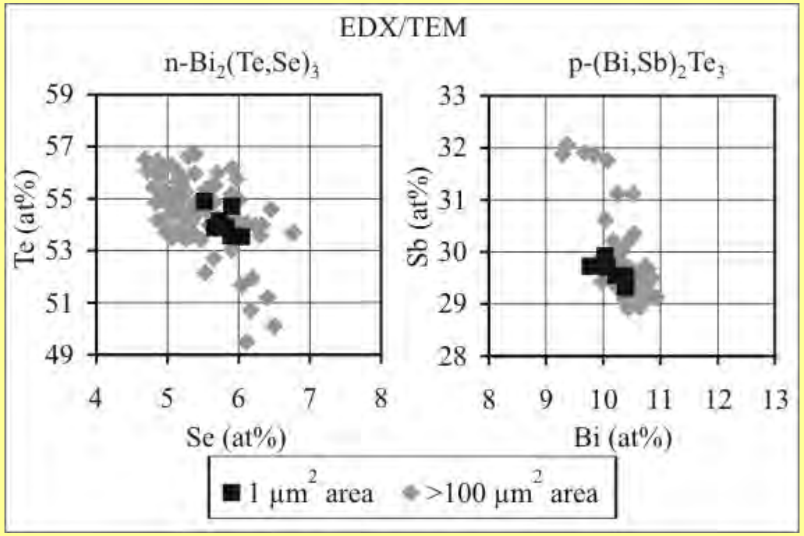
EPMA: lateral resolution 1 µm



SPM: lateral resolution 20 µm



EDX in the TEM: lateral resolution 50 nm



→ **variations in stoichiometry on the micrometer scale**

±1.5 at% Te/Se in n-type $Bi_2(Te,Se)_3$

±1.5 at% Bi/Sb in p-type $(Bi,Sb)_2Te_3$

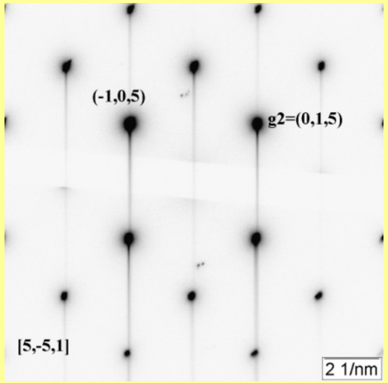
→ **variations in thermopower on the micrometer scale**

-192±9 µV/K

N. Peranio and O. Eibl, „Quantitative EDX microanalysis of Bi_2Te_3 in the TEM", Phys. Status Solidi A 204, 3243 (2007).

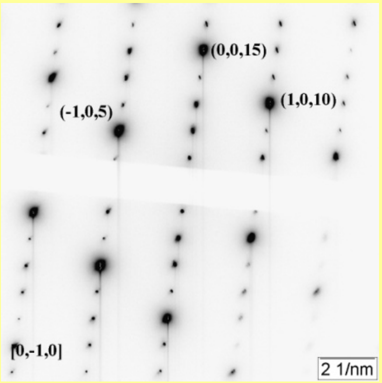
Stereomicroscopy (tomography):
acquisition of two-beam images+ tilt series
→ character of dislocations

pole 2



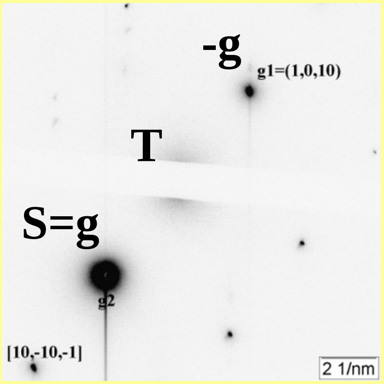
50° tilt

pole 1

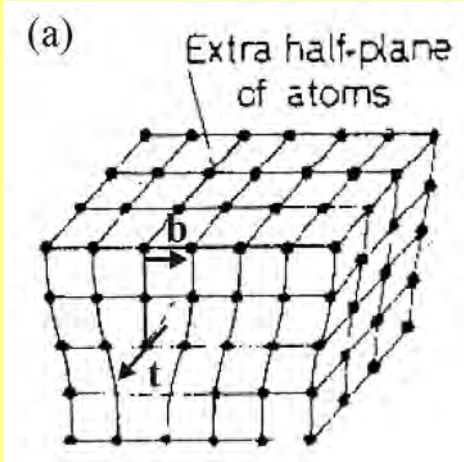


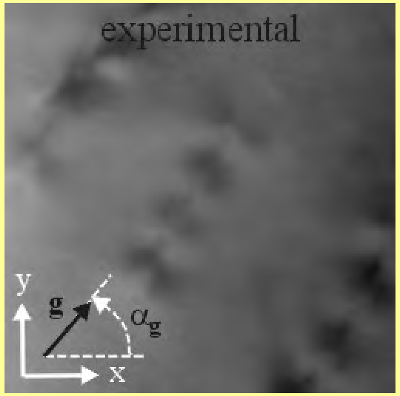
10° tilt

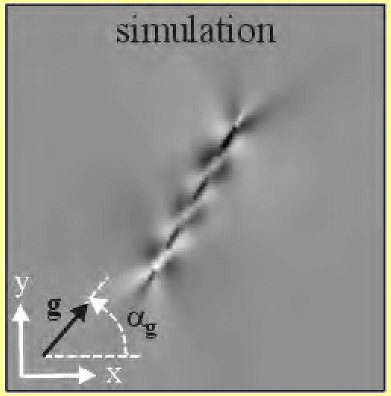
Two-beam condition
for Bragg-reflection **g**



Dislocation:
bending of lattice planes **g**
→ strain contrast under two-beam condition



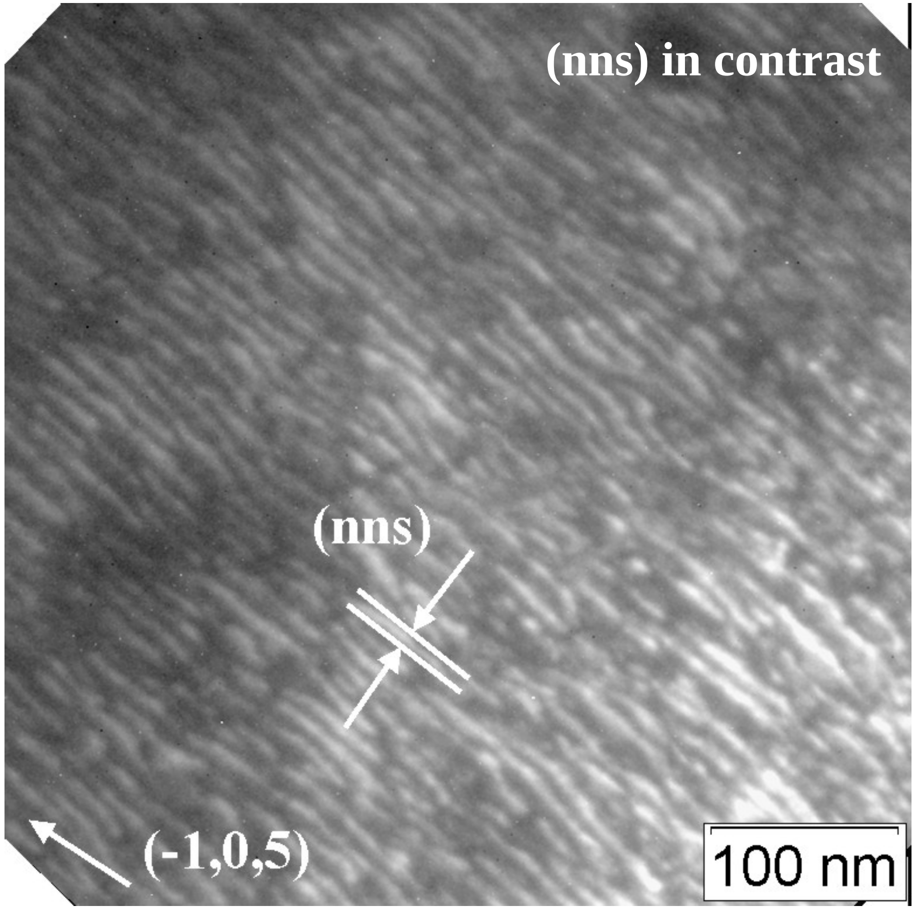


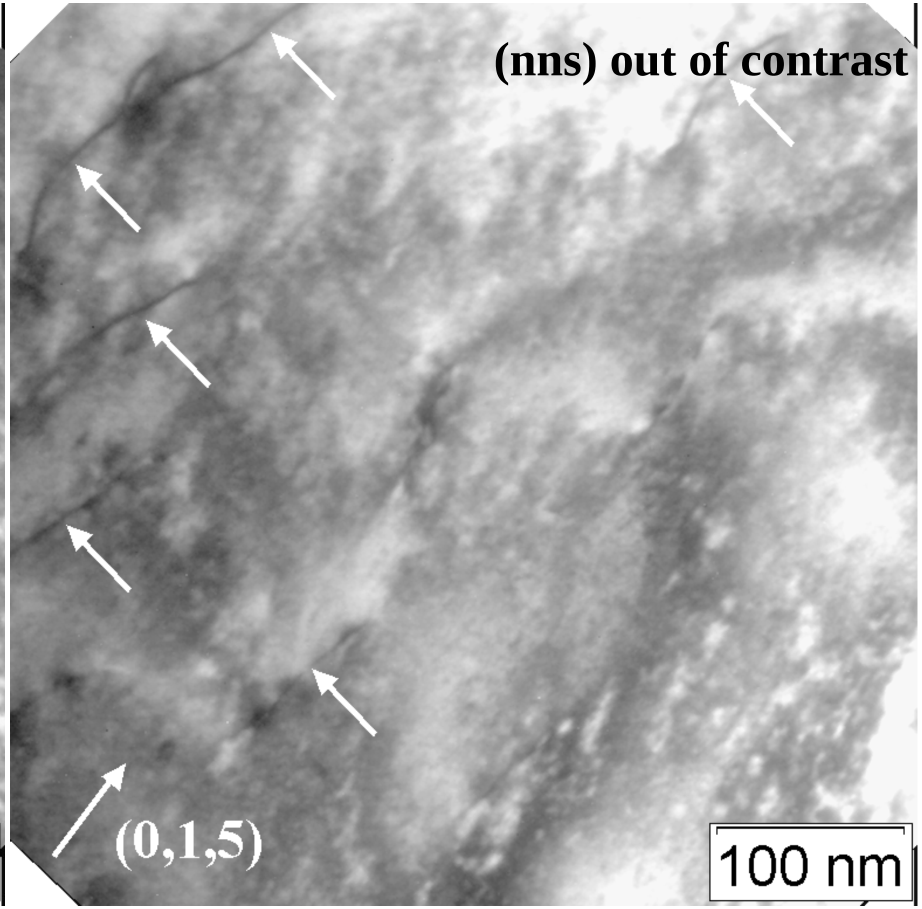


Dislocation (strain field) out of contrast:

$$\vec{g} \cdot \vec{b} = 0 \qquad \vec{g} \cdot \vec{u} = 0$$

nns and gliding dislocations in n-type Bi_2Te_3





structural modulation (nns):
sinusoidal displacement field
$\mathbf{u} = \mathbf{u}_0 \cdot \sin(\mathbf{q} \cdot \mathbf{x})$
wavelength 10 nm,
wave vector **q**: (1,0,10),
displacement vector $\mathbf{u}_0$: [-10,-5,1]

reflection g	(nns) in contrast ?
(-1,0,5)	yes
(0,1,5)	no (g*u=0)
(1,0,10)	no (g*u=0)

gliding dislocations
in the basal plane
density $10^9 cm^{-2}$
Burgers vector [1,1,0]

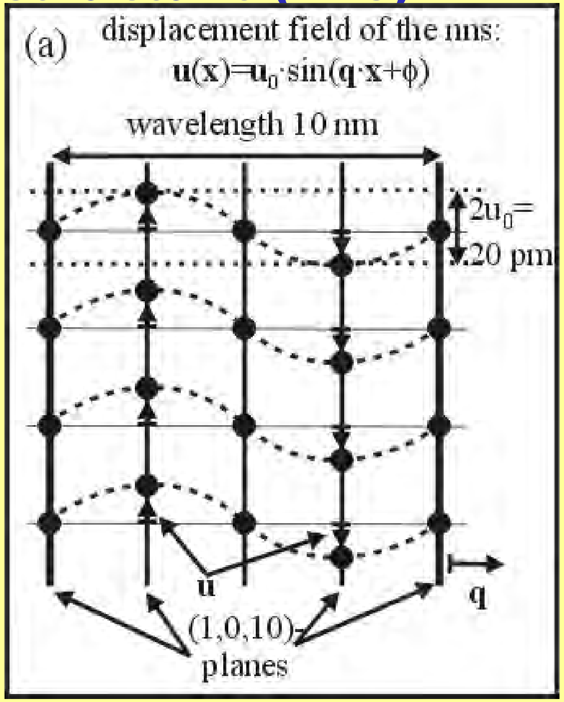
Structure model for the natural nanostructure (nns)

1. A structural modulation (nns) is superimposed to the average structure and can be imaged using the {-1,0,5} reflections.

2. The nns is of general character for Bi_2Te_3 materials: n-type and p-type bulk materials.

3. The origin of the nns is a pure structural modulation with wavelength of 10 nm, wave vector {1,0,10}, displacement vector <5,-5,1>, and an amplitude of 10 pm.

4. Rejected models for the nns: chemical modulations and ordered network of non basal plane dislocations



Thermoelectric properties and the nns

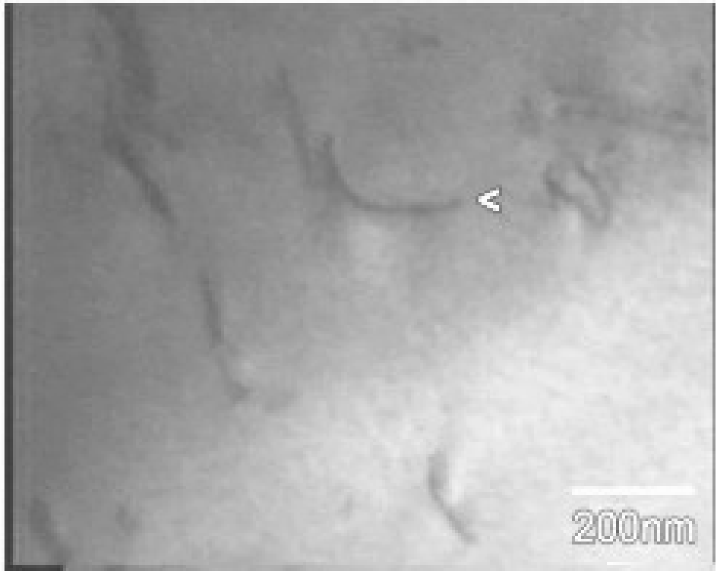
1. Bi_2Te_3 shows a λ_{latt} like highly disordered materials, the nns is a significant structural disorder. Lattice thermal conductivity should be decreased due to phonon scattering on the sinusoidal strain field of the nns.

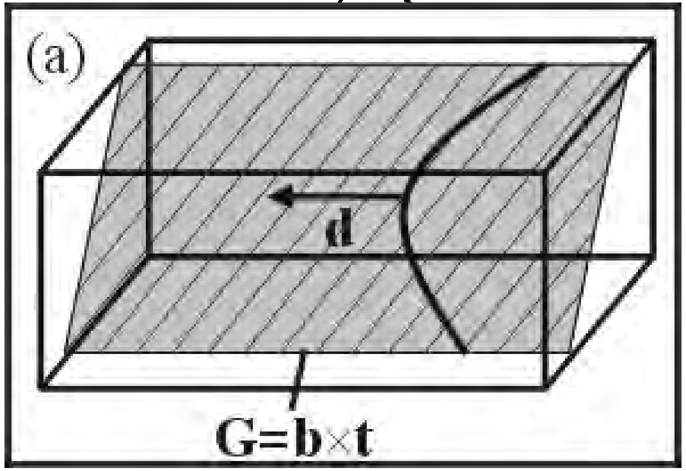
2. The nns should yield a one-dimensional or zero-dimensional behaviour and anisotropic transport coefficients in the basal plane.

3. The number of nns and thereby the thermoelectric properties might be controlled by the thermal history of the sample.

N. Peranio and O. Eibl, „Structural modulations in Bi_2Te_3“, J. Appl. Phys. 103, 024314 (2008)

Gliding dislocations in Bi_2Te_3 bulk





Burgers vector **b,** line direction **t,** glide plane **G**, direction of motion **d**

→ gliding at room temperature and without applied shear stresses
→ an activation energy has thermally to be overcome to start and maintain motion
→ basal plane as glide plane, b=<1,0,0>

Lattice thermal conductivity at 3 K

λ_{latt} according to literature	transport theory for isotropic solids: $$\lambda_{latt} = \frac{1}{3} C \cdot v \cdot l_{ph}$$	phonon mean free path and dislocation density N: $$l_{ph} = \frac{0.455}{\gamma^2 k_D} \frac{\theta_D}{T} \frac{1}{b^2 N}$$	
230 W/mK	729 µm	832 µm	→ agreement
15 W/mK	48 µm	832 µm	→ no agreement → more sources for phonon scattering

Gliding dislocations in Bi_2Te_3

1. Dislocations in the basal plane with a high mobility at room temperature were found. The motion was induced by heating with a focused electron beam. External stresses were not applied.
2. Stereomicroscopy investigations combined with image simulations yielded basal plane dislocations with a density of 10^9 cm^{-2} and Burgers vectors <1,1,0>.
3. Phonon scattering on dislocations in Bi_2Te_3 reduces the lattice thermal conductivity.

N. Peranio and O.Eibl, „Gliding dislocations in Bi_2Te_3 materials“, Phys. Status Solidi A 206, 42 (2009).

Summary

Expected:

1. Chemical analysis established in TEM and EPMA
2. Density and character of dislocations determined
3. Specimen preparation established, particularly thin films in cross section
4. Imaging of superlattices

Unexpected:

1. nns discovered and character explained: scattering center for phonons, role of the superlattice
2. Variations in stoichiometry: local changes of carrier density
3. Gliding dislocations at room temperature : scattering center for phonons
4. Bending of superlattices due to threading dislocations: carrier mobility

Outlook

SPP 1386:

"Nanostructure, excitations, and thermolectric properties of Bi_2Te_3-based nanomaterials"

Thank You !!!

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