Towards Alternative Energy Sources: Structure of Thermoelectric Nanomaterials

Thermoelectric materials allow the conversion of a thermal gradient into a gradient of electrical potential

The decrease of fossil fuel resources has motivated many research groups to seek technologies for the utilization of alternative energy sources. Solar cells operating at 20% efficiency and covering 0.1% of the Earth's land area would be sufficient to supply the worldwide yearly energy requirement . The Sun as an energy source can also be used by thermoelectric (TE) modules which directly convert solar heat into electricity. The advantage of TE modules compared to photovoltaic (PV) solar cells is that TE modules utilize the whole solar spectrum (IR, UV and visible radiation), while PV cells only use the UV–Vis part of the spectrum Low thermal conductivity is a prerequisite for effective thermoelectric materials, and the challenge is to limit the transport of heat by phonons, without simultaneously decreasing charge transport. Zinc antimonides, like Zn_4Sb_3 and ZnSb are well known thermoelectric materials as they have a high potential as the p-type leg of thermoelectric couples and are used to generate electric power in a temperature range of 300K to 700K. The thermoelectric power factor of ZnSb is high enough to make it a attractive thermoelectric material. A solution-phase technique was devised for synthesis of Zn_4Sb_3 nanocrystals as a precursor for phase segregation into ZnSb and a new Zn-Sb intermetallic phase, $Zn_{1+\delta}Sb$, in a peritectoid reaction. Crystallographic investigation of the synthetic modules was performed using electron diffraction, as single-crystal X-ray diffraction techniques cannot be applied to nanostructures and powder X-ray analysis meets serious problems when the size of the crystals is below 50 nm and there is the probable presence of different phases in the sample.

The challenge:	aggregated of polyphasic nanoparticles; low quality X-Ray pattern
Solution:	3D diffraction Tomography with precession diffraction

The TEM data show clearly the presence of at least two crystalline phases. The unit cell parameters of the first phase, ZnSb, were determined with the 3D diffraction tomography data and subsequently refined against powder X-ray diffraction data. They agree well with the known structure. The systematic extinctions on the 3D reciprocal spare are compatible with the space group Pbca and the obtained structure model exhibits a close match to the known crystal structure of ZnSb with errors in atomic positions of 0.02 Å for Sb and 0.05 Å for Zn.

solar cells

The 3D reconstructed data set recorded for the unknown second phase, $Zn_{1+\delta}Sb$, shows that the cell parameters did not match those of any known Zn-Sb phase, even if the new phase has to be strictly geometrically related with rombohedral Zn_6Sb_5. A careful inspection of several zone axes using beam precession shows that the only true symmetry element present is the inversion center, and the structure is triclinic. Processing 3D diffraction tomography & PED data using Sir2008 the structure was finally solved in space group P-1. A fully kinematical approach was used, and no correction was applied to the data set.

Ab initio structure solutions were performed for both the phases on the basis of electron diffraction data obtained by ADT. Precession electron diffraction data were necessary for the more complex phase $Zn_{1+\delta}Sb$. This new $Zn_{1+\delta}Sb$ phase crystallizes with a hexagonal pseudosymmetry in the triclinic space group P-1 and shows strict relations with both $Zn_{13}Sb_{10}$ and ZnSb. Remarkably, the structure was obtained by single- crystal analysis of a 50 nm particle, and the solution was achieved *ab initio* in one step with a fully kinematical approach.

Crystal Structure

$Zn_{1+\delta}Sb$

Triclinic P-1
a=15.31 Å
b=15.51 Å
c=7.81 Å
α= 88.87°
β=89,42°
γ=119.4°

Experimental data

tilt range: ±38° step: 1°
No ind. reflections: 3651
No ind. atoms: 30
R = 36.19 %

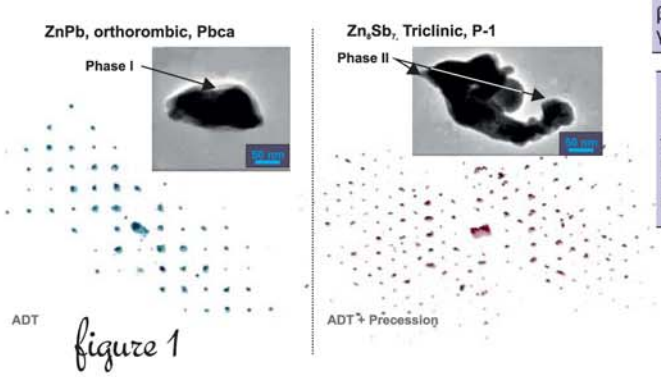

figure 1

Nanocrystals Area used for Structure Analysis and the Corresponding 3dDiffraction reconstruction of Phase I (Left) & Phase II (Right)

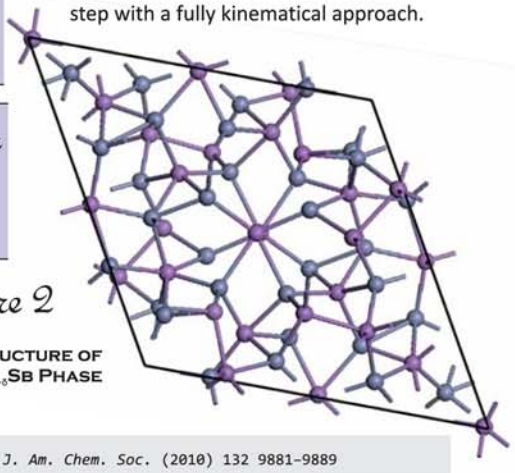

figure 2

Crystal Structure of the $Zn_{1+\delta}Sb$ Phase

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