Facile bulk synthesis of π-cubic SnS

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ABSTRACT: The cubic modification of binary tin sulphide SnS has gained significant interest as an earth-abundant, low-toxic solar absorber material with a bandgap close to the optimal value for the conversion of sunlight. We herein report a surprisingly simple synthesis for the metastable material, which will allow more elaborate characterization methods to be used on this material and present the first full powder refinement of the material along with some preliminary results on the optical and thermal stability properties.

The focus in the development of alternative (i.e. non-silicon based) solar cell absorber materials has, in recent years, shifted from the sole concentration on materials with a suitable bandgap onto the consideration of "secondary" aspects such as low toxicity and earth-abundance of the composing elements. One such material considered as promising candidate is the metastable π-cubic SnS, which has been demonstrated as solar absorber material using thin films.[1] Given the relatively large unit cell and the unusual space group symmetry of the material, earlier reports of the material wrongly assigned this material as zincblende type,[2-4] but more recent studies using electron diffraction[5] as well as Rietveld refinement of X-ray diffraction patterns taken on thin films[6] identified the structure to be in the cubic space group $P2_13$. This was further confirmed using first principles calculations, which also outlined the metastable nature of π-cubic SnS lying approx. 2 kJ/mol per formula unit above the orthorhombic herzenbergite structure.[7]

Nonetheless, the material has been demonstrated as a promising solar absorber material but synthesizing phase pure bulk material remains challenging. We herein demonstrate such a synthesis along with some preliminary characterization in order to stimulate the research on this most promising material.

Regarding the different successful syntheses of "zincblende" SnS, it appears that the crystallization of nano-sized powders is most effective, which may be due to a size effect. While most prior syntheses used surfactants such as oleylamine,[5] our synthesis makes use of ethylene glycol both as solvent and surfacting agent. To produce π-cubic SnS, we dissolved $SnCl_2$, $Zn(NO_3)_2{\cdot}6H_2O$ and thioacetamide in a molar ratio of 1:1:4 in ethylene glycol. The solution was heated to a maximum temperature of 80 °C for 10 min to produce a black precipitate (A more detailed description may be found in the electronic supplementary information: ESI). The powder proved to be crystalline but both the strong peak broadening observed in the X-ray diffraction (XRD) pattern as well as the scanning electron microscopy (SEM) imaging (figure 1) advocate for a small particle size. The role of $Zn(NO_3)_2{\cdot}6H_2O$ is not yet fully understood, but it appears to act as a catalyst in the reaction. Without its addition, we do not observe the formation of π-cubic SnS but rather poorly crystalline powders that are most likely orthorhombic *Pnma* SnS.[8] One could easily assume that Zn may partly replace Sn in the structure to form a ternary sulphide, but careful SEM/EDX mapping of the product however, showed no evidence for Zn inclusion in the sample. However, EDX mapping evidences an isotropic Sn and S distribution within the sample (ESI) and therefore

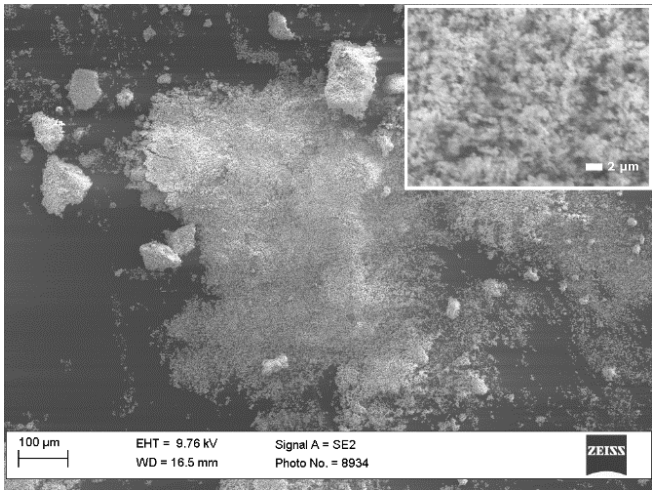

Figure 1. SEM image of π-cubic SnS as obtained from the described synthesis.

seconds the formation of a single-phase binary compound. Moreover, the Sn:S ratio as measured by EDX of 1:0.93 allows, when taking the semi-quantitative nature of the method into account, to assume the stoichiometry of the product as SnS. This synthesis therefore has the potential to allow the facile production of larger amounts of cubic SnS in order to run more sophisticated characterization techniques. The powder allowed us to perform the first Rietveld refinement on a powder sample and we could confirm the overall structure as determined from electron diffraction and thin-film XRD.

The powder X-ray diffraction patterns shows significant peak broadening (figure 2), which is indicative of a very small crystallite size. Furthermore, the peak shape is purely Lorentzian and hence indicates that the peak broadening is due to the small crystallite size. Applying the fundamental parameter approach during the Rietveld refinement using Jana2006[9] (table 1) yielded in an apparent crystallite size of 37(6) nm. The broad peaks and the comparably complex pattern with a significant background contribution are making a Rietveld refinement cumbersome and afford the introduction of some constraints, namely fixing the U_{iso} values of the different atoms to a common value, in order to achieve a stable refinement. Still, we were able to determine the atomic positions reliably and therefore examine the bonding situation. As reported, the compound crystallizes in the cubic space group $P2_13$ with a cell parameter of a = 11.568(3) Å. This cell parameter is slightly smaller than what was found using electron diffraction (a = 11.7 Å)[5] and thin-film XRD (a = 11.603 Å)[6] but larger than the cell parameters found from first-principles calculations (a = 11.506 Å)[7]. The difference to the cell parameters observed by thin film diffraction may be due to the considerable stresses and strains that can occur in thin film samples. The Sn and S atoms are distributed on four crystallographically independent positions, each. This is despite a similar coordination of all the atoms of each element and may be due to the strongly asymmetric bonding in Sn^{II} due to its lone pair. Rationalizing the bonding situation in this compound may indeed be clue to understanding the atomic arrangement, which could be regarded as extremely distorted rocksalt type structure (figure 1, inset)[7] with three Sn-S distances being considerably shorter (2.57(9) Å– 2.8(2) Å) than the remaining three distances (all over 3.1 Å). Conventionally, the Sn coordination could therefore be considered tetrahedral including the lone pair occupying the fourth corner. This is, however, somehow questionable when regarding the S–Sn–S angles of the three bonding Sn–S contacts, which are very close to 90° (87(6)°–92(4)°). The Sn–S–Sn angles on the other hand are stronger distorted (97(5)°–106(5)°) and therefore lie between the angles expected for octahedral and tetrahedral coordination. In addition, considering the sulphur bonding as electron-precise covalent bonding has the severe problem that a sulphur atom with three bonds would count 9e$^-$ valence electrons and should hence not be stable. It will therefore be an important task for the future to second theoretical considerations on the bonding in these

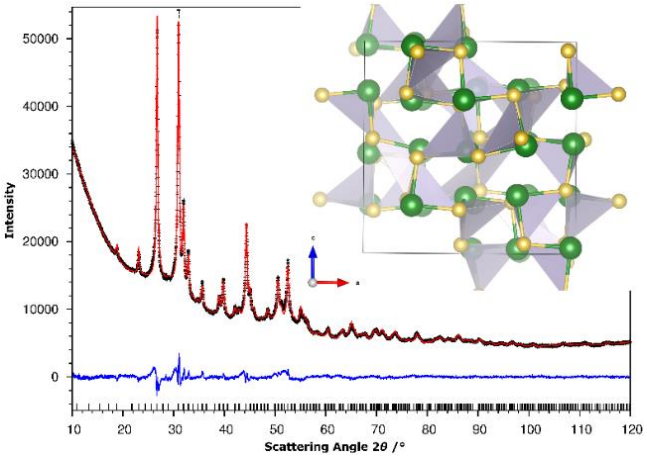

Figure 2. Experimental (black crosses) and calculated pattern (red line) of the Rietveld refinement. The difference I_{obs}-I_{calc} is given as blue line and the theoretical peak positions as black stacks. Inset: View of the crystal structure of π-cubic SnS (Sn: green, S: yellow) along the crystallographic b-axis.

Table 1. Refinement parameters for π-cubic SnS

Formula	**SnS**
Crystal System	cubic
Space group	$P2_13$
a /Å	11.568(3)
V /Å^3	1548.0(8)
Z	32
ρ /(g/cm^3)	5.1753
R_p; wR_p	0.017; 0.024
Goof	2.41
R_{obs}; wR_2(all)	0.044; 0.062

materials by careful local spectroscopy in order to elucidate the exact coordination and bonding situation in these compounds. Doing so will potentially allow to understand the unique properties of the material and hence allow its targeted development into future application.

In order to examine the phase stability of the product, we studied the thermal behavior using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA). The DTA shows an exothermic signal at 320 °C (figure 3) which is most probably due to the transformation of the metastable π-cubic SnS to the thermodynamically stable herzenbergite structure. The latter could also be identified as the main product of the thermal decomposition using powder X-ray diffraction (ESI). Some supplementary reflection did, nevertheless, indicate the presence of a second, minor phase, which could be identified as Sn_2S_3.[10] Given the different stoichiometries of SnS and Sn_2S_3, the formation of Sn_2S_3 has to go along with the formation of another tin containing phase or the evaporation of tin from the reaction mixture. The small, but constant weight loss during the reaction (roughly 5 % weight loss over the

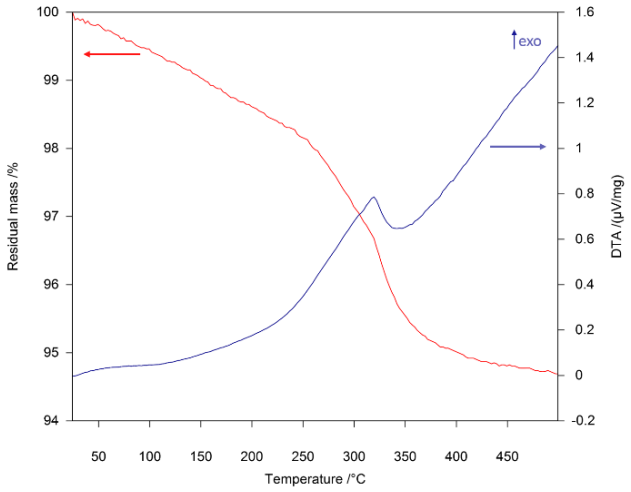

Figure 3. Combined thermogravimetry (red curve) and differential thermal analysis measurement (blue curve) of π-cubic SnS.

temperature range 25-500 °C correspond to a weight loss of 0.6 mg from 12 mg sample) could be due to evaporation of residual solvent or, indeed, the evaporation of tin from the sample, especially at elevated temperatures. Assuming stoichiometric SnS as starting material, the loss of 5 % weight would correspond to the formation of 13.8 wt.-% Sn_2S_3, which is confirmed by a quantitative Rietveld refinement of the final reaction product, where the gravimetric phase ratio SnS:Sn_2S_3 was determined as 86(2) %:14(1) % (ESI). To further confirm the materials properties of π-cubic SnS, we performed a UV-VIS absorption measurement in transmission (ESI), which shows a bandgap at around 1.7 eV, consistent with previous studies as well as theoretical calculation on this material.[2,11]

In conclusion, we have demonstrated a surprisingly simple method for the synthesis of π-cubic SnS, which has the great potential to combine the advantages of perovskite solar cells, namely simple processing and highly absorbing materials with an earth-abundant and low toxic material. We greatly encourage the research community to consider this material for further research directions, especially with regards to thermal and photo-stability and structural properties.

ASSOCIATED CONTENT

Supporting Information. Experimental details, Rietveld refinement details for π-cubic SnS and post TG/DTA o-SnS/Sn_2S_3 mixture, EDX mapping and UV-VIS spectrum are given as supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

XRD, X-ray diffraction; SEM, scanning electron microscopy; ESI, electronic supporting information.

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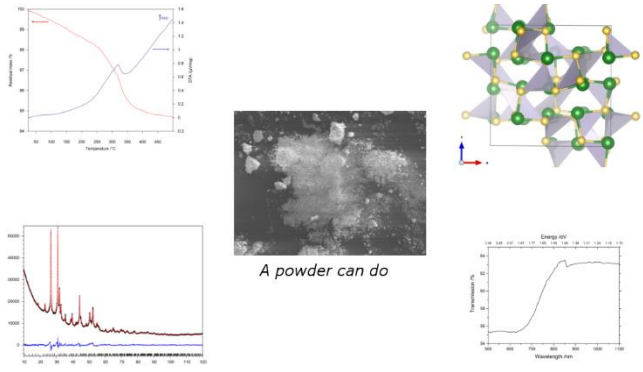

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TOC synopsis: π-cubic SnS is a promising thin-film solar absorber, but powder samples are necessary to understand all of its properties. We herein present a simple synthesis method for π-cubic SnS powder and demonstrate some preliminary results of the structural and chemical characterization.