

Combinatorial Separation of Cd and Te from CdTe via Chemical Vapour Transport with Sulfur and Air/Methane Treatment for the Recovery of Critical Resources from Thin Film Solar Cells

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Dedicated to Prof. Dr. Michael Binnewiest in Memoriam.

Elemental Te and Cd are successfully recovered from CdTe via a combinatorial process involving chemical vapor transport (CVT) using sulfur as transport agent giving elemental Te being deposited. Separation is successfully enabled by the first process for CVT of Te starting with CdTe. Cd is subsequently recovered by an oxidation of the formed CdS to CdO followed by reduction to Cd metal with natural gas, in which Cd can also be separated via the gas phase. Hereby, the process addresses the main critical elements of the active material in thin film CdTe solar cells regarding both, scarcity and toxicity. Both,

closed and open systems were investigated displaying more or less thermodynamic control of the system. Transport rates were determined for the closed system as well as for an open system working with sulfur vapour at moderate temperatures below and close to the boiling point of sulfur. Excellent purity of tellurium was achieved already by the initial transport, leading to low Cd²⁺ concentrations in the obtained Te being below the quantification limit of microwave plasma-atomic emission spectroscopy (MP-AES) ($\ll 0.05$ wt%).

Introduction

CdTe is an important material used for thin-film solar cells because of its chemical stability and optimal band gap of about 1.5 eV, first introduced in 1972 by Bonnet and Rabenhorst for a CdTe/CdS heterojunction.^[1] CdTe is thermally and chemically stable, which enables the production of thin film solar cells with a variety of methods and designs.^[2] The market for photovoltaic modules is dominated by silicon-based panels (> 95% in 2021) and the rest consists of thin-film solar cells, which are mainly CdTe and copper indium gallium selenide (CIGS) cells. Therefore, CdTe-based modules make up only a small percentage of the global market.^[3] However, CdTe thin film solar cells are especially interesting by means of sustainability, as their

production leads to a shorter energy payback time, lower water consumption and lesser greenhouse gas emissions compared to other photovoltaic technologies.^[31]

The steady installation of more photovoltaic plants and the expected lifetime of the modules of 20–30 years will lead to a dramatic increase in photovoltaic waste of up to 78 million tonnes in 2050, which need to be recycled.^[3] This includes Te and Cd from CdTe, as both elements are already considered critical and are toxic along with their compounds. However, the thin layer of semiconductor material of only 2–8 μm leads to low demand of only 1–6 mg CdTe per cm^2 of the solar cell.^[7–8] As the actual solar cell contains < 1% CdTe, separation from the soda lime glass (95%) and polymers (4%)^[9] is preferable for a chemical recycling process.^[10]

The main source for Te is as a byproduct from copper refining, so the amount of tellurium obtained today depends strongly on the amount of produced copper. Additionally the annual production of cadmium is around 40 times higher than the amount of tellurium, which also makes a recovery highly desirable.^[3–6,9,11] Recycling of cadmium is nevertheless important due to its hazardousness against environment and health.^[31]

Conventional recovery methods consume high amounts of chemicals, strong bases for alkaline leaching, strong acids for acidic leaching and additional reactants for precipitation as well as further purification steps.^[12] One reported method for the recycling of CdTe from photovoltaic waste contains a leaching step with H₂SO₄ and H₂O₂ followed by separation of Cd and Te through a cation exchange resin to reach a purity of 99.99%.^[13]

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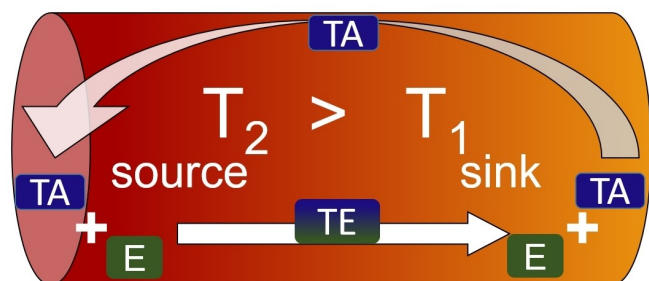
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Recently, a new recycling method was introduced by Yang et al. replacing the leaching procedure by a vacuum distillation. CdTe is oxidised with S to elemental Te and CdS at 400 °C and the Te is separated by vacuum distillation 650–850 °C for 40 min. This is followed by two additional heating steps for the removal of Cd at 450 °C and removal of S at 400 °C to reach a purity of Te of 99.97% and a recovery rate of 99%.^[14]

In contrast to the large consumption of chemicals used for conventional methods, such as hydrothermal treatments involving leaching processes, chemical vapour transport (CVT) requires a lower amount of additional chemicals. These are called transport agent and react at elevated temperature with a specific element to form a new gaseous species in an equilibrium reaction, which is then transferred to another place with a different temperature to induce the back reaction.^[15] This is used to separate the element Te in the reported process. In a closed system, the transport agent can subsequently cycle and carry out the reaction multiple times, minimizing the amount that is needed for CVT (Scheme 1). Another option more suitable for industrial use is CVT in an open flow system where new transport agent is added to the system constantly via one end of the tube and leaves it at the other end after the reaction, from which it can be also cycled back to the starting point of the reaction and used multiple times. In both cases the place where the gaseous species is formed is called source and the place for the back reaction is called sink. Both places have specific temperatures, T_1 and T_2 , with T_2 being the higher one, which is not necessarily the source, depending, if the transport reaction is exothermic or endothermic (as it is here).

The CVT of Te with S was demonstrated in 1976 by M. Binnewies et al., in a closed quartz ampoule. Several compounds were identified via mass spectrometry as gaseous species: $\text{TeS}_X^+(\text{g})$ ($X = 1, \dots, 7$) and $\text{Te}_2\text{S}_Y^+(\text{g})$ ($Y = 1, \dots, 6$).^[16] Taavitsainen et al., synthesized octameric chalcogen rings of S, Se and Te, confirmed by NMR-spectroscopy, and calculated their stability via second-order Møller-Plesset perturbation theory.^[17] Sulfur rich hetero chalcogen rings seem to be most stable, and also Te and Se in the same sulfur ring were calculated to be possible especially when they are adjacent to each other. The calculations confirmed that the CVT of Te with S, demonstrated



Scheme 1. General principle of a CVT. An element (E) reacts with the transport agent (TA) to form the transport-effective species (TE) in an equilibrium reaction. In a T-gradient, TE is moved in the gas phase to a point, where the equilibrium is reversed. A more detailed depiction is shown in Figure 2 a) for the closed system used in this study and in Figure 2 b) for the applied open flow system.

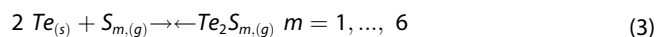
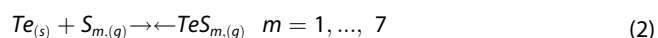
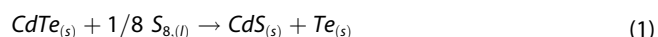
by Binnewies et al., is based on such hetero octameric chalcogen rings as transport effective species.^[16] Another chemical transport of Te was reported in 1971 from J. Burmeister et al., where I_2 was used as a transport agent in quartz ampoules with TeI_2 as gaseous species yielding single crystals of Te.^[18] Iodine was likewise used by Hotje et al. for the transport of CdTe in a temperature gradient of 900 to 800 °C to achieve CdTe crystals.^[19] Schäfer et al. compared the crystal morphology of Te in dependence of different types of transport reactions. Sublimation of Te in vacuum lead to long needles, CVT with sulfur resulted in square shaped crystals and CVT with iodine gave compact intergrown crystals.^[20]

CVT processes are also known for other binary tellurides. Schöneich, et al. performed theoretical and experimental studies using a transport balance for the transport of Sb_2Te_3 and Bi_2Te_3 and the respective selenides Bi_2Se_3 and Sb_2Se_3 with iodine from 500 to 450 °C.^[21]

Altogether, only a limited number of reports was published on the CVT of Te with S, and a direct transport reaction from CdTe to elemental Te has not yet been utilized. This includes the combination of such CVT with a follow-up procedure also covering the element Cd, which is presented in this work, too.

Results and Discussion

A combinatorial method for the recovery of both, Te and Cd from thin-film solar cell waste starting from CdTe was investigated in this work by combination or several redox reaction steps with chemical vapor transport and gas phase utilization. The method described in this work was patented before publishing.^[22] The separation starts with the oxidation of CdTe with sulfur to form the elemental tellurium (Equation (1)), which can then react with additional sulfur to enable CVT-reaction. The fundamental equilibrium reactions for the CVT in which the tellurium containing sulfur rings are formed are therefore identical to the chemical transport of the element Te with S (Equations (2) and (3) according to [12]).



The mass of the transported Te was used for calculating the yield and transport rate for different combinations of temperatures at the site where the starting materials are placed (source) and the one where the transported product is deposited (sink). The CVT was investigated for ampoules representing a closed system with equilibrium conditions as well as for flow tubes, which represent an open system where no full chemical equilibrium is reached. The latter design is also more suitable for a continuous process and therefore an industrial application.

The product at the sink is transported elemental Te, while the remaining components at the source are afterwards used

for the separation of Cd. This was achieved in two steps, the first one is the oxidation of CdS to CdO with air, followed by a reduction of CdO to Cd with methane causing the elemental Cd to evaporate and as a consequence get separated from the remaining parts of the solar cell. These were in this case In_2O_3 and SnO_2 as model compounds for ITO, which covers the CdTe layer in the solar cell.

The products were analysed for their purity with powder X-ray diffractometry (PXRD), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), microwave plasma atomic emission spectroscopy (MP-AES). PXRD was used as a quick method to check for phases and crystallinity of the samples. SEM-EDX can detect the elements which are present with a lower detection limit compared to PXRD close to the surface. MP-AES was used for the detection of trace amounts of Cd. Thermal analysis by differential scanning calorimetry (DSC) and differential thermal analysis with simultaneous thermogravimetry (DTA/TG) were applied to further investigate the important processes in the temperature region relevant for a recycling of CdTe via the gas phase/CVT.

Recovery of Tellurium

The recovery of Te (and Cd) from CdTe via the gas phase combines several processes and reactions which have to be well understood for a successful result. These are the redox reaction (Equation (1)), the formation of the transport active species (Equation (2) and (3)), evaporation of S, Te and Cd as well as several phase transitions of the components. Additionally, it is important to know whether there are any other side reactions taking place or not.

The complete process of redox reaction and CVT can be achieved in either a closed system or an open system, which are the two main methods for CVT. Both techniques have to be investigated separately due to their unique features.

Valuable results to determine processes occurring by heating and cooling substances or mixtures in a certain temperature region were acquired from additional differential scanning calorimetry (DSC) and simultaneous thermal analysis (STA), combining thermogravimetry (TG) and differential thermal analysis (DTA) by detecting either mass loss or gain (TG) or energy uptake or energy release (DSC/DTA). DSC measurements were conducted in small closed quartz ampoules, which could withstand higher pressures and therefore resemble the conditions of a closed system but without defined sides for source and sink.

Low-Temperature Borders for the Use of Sulfur and for the Redox Reaction of CdTe Under Exclusion of Side Reactions

In principle, the boiling point of sulfur, $444^\circ\text{C}^{[23]}$ marks the temperature, at which the element is fully present in the gas phase. However, STA shows that S starts evaporating already at 300°C and in a system with a mild gas flow, it enters the gas phase completely already below the boiling point (Figure S26), enabling a recovery process to be conducted at temperatures below the actual boiling point of sulfur making it more energy saving. As a result, the temperatures for the transport reactions were determined to be suitable already between 350 to 425°C .

In addition to volume reactions, again, thermal analysis was applied to directly monitor the reactions of CdTe with S. DSC of a reaction mixture of CdTe and S (Figure 1a) reveals the signals for the melting point of S (108°C , signal 2, endothermic) and for the formation of polymeric S (152°C , signal 3, endothermic). Additionally, a signal at 350°C (5, exothermic) indicates the redox reaction between CdTe and S. The absence of other signals indicates that there are no unwanted reactions taking place in the temperature range from room temperature up to 500°C , which is more than sufficient for the CVT. For comparison, pure commercially available CdTe was also inves-

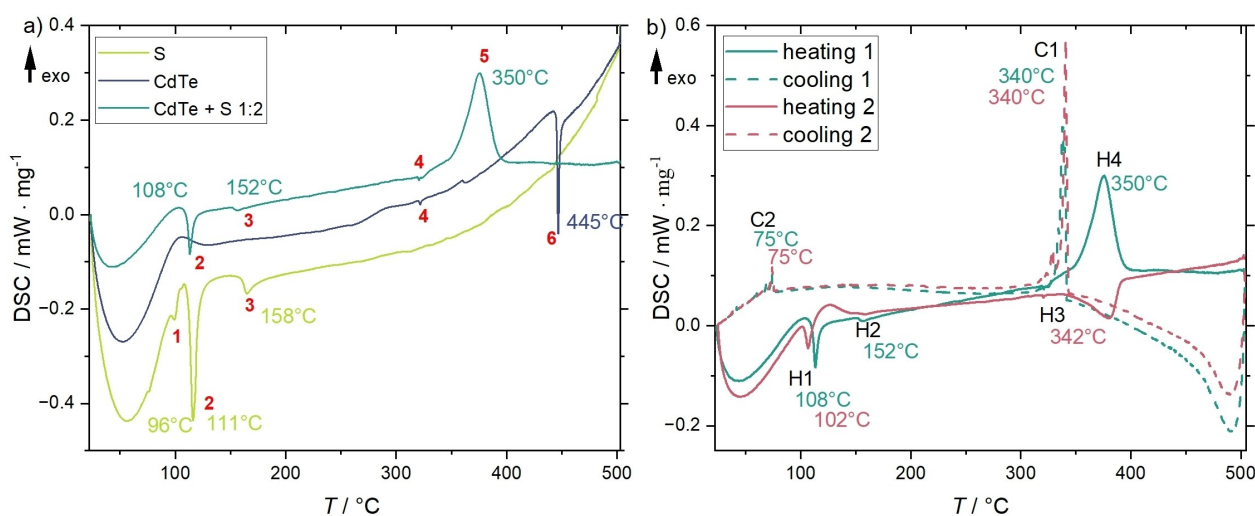


Figure 1. a) DSC of pure sulfur (green), pure CdTe (blue) and a mixture of S and CdTe with 2 times excess of S (turquoise) in a closed system. b) DSC of a mixture of CdTe and S in a closed quartz ampoule with heating curves (straight) and cooling curves (dashed) of the first (turquoise) and second (red) run, signals in the heating curve (H) and in the cooling curve (C).

tigated by DSC in the same temperature range indicating small impurities of elemental Cd and Te by the melting points of Cd (321 °C, signal 4, endothermic) and Te (445 °C, signal 6, endothermic) (Figure 1a).

The signals observed in a comparison DSC measurement of sulfur correspond fully to the anticipated thermal properties (Figure 1a). These include the phase transition of rhombic sulfur to monoclinic sulfur (96 °C, signal 1, endothermic), the melting point of monoclinic sulfur (111 °C, signal 2, endothermic) and the formation of polymeric sulfur (158 °C, signal 3, endothermic). The identification of all signals is summed up in Table 1.

In addition, DSC of CdTe with S was carried out also in cycles in order to distinguish chemical reactions occurring only on the first heating from phase transformations occurring in the system also after the first heating cycle. The investigation is shown in Figure 1b for heating tagged with 'H' and cooling with 'C'. During the first cooling at there is a strong signal (340 °C, C1, exothermic) showing the solidification of Te from the melt which is in accordance with the phase diagram of Te + S.^[26] The signal (75 °C, C2, exothermic) is indicating the solidification of S. The second heating run shows melting of S at a slightly lower temperature (102 °C, H1, endothermic) due to the mixing with elemental Te. The formation of polymeric S is not clearly visible anymore and at 342 °C (H3, endothermic), a signal is showing the melting with dissolution of Te in S instead of the redox reaction. This is also in accordance with the phase diagram indicating a high content of S can reduce the melting temperature of a mixture of Te and S considerably. The liquid phase has a higher content of S compared to the solid phase leading to the solid getting depleted in S content during melting, which increases the melting point. Therefore the signal (342 °C, H3, endothermic) for melting of the Te–S mixture is broader compared to the one for the melting of pure sulfur (102 °C/108 °C, H1, endothermic), which is sharp.^[26] Its exother-

mic signal H4 does not appear anymore because the redox reaction between CdS and Te already took place fully during the first heating run and is not reversible. The second cooling cycle is identical to the first run.

This overall outcome is beneficial for the CVT because Te has to be in elemental form to take part in it and this is also possible at rather low temperatures > 350 °C, as the redox reaction already proceeds at this temperature. The identification of all signals is summed up in Table 2. In principle, and although sharp, signal (H3, exothermic) in Figure 1b could also indicate another process, such as the rapid formation of gaseous species, e.g. determine, if this is a signal for a melting point or for the formation of gaseous species, mixtures with four different ratios of Te and S were investigated by DSC. The results for the heating curves are shown in Figure S27, the ones for the cooling in Figure S28.

The experiments with a high content of S give the signals for the phase transition from rhombic to monoclinic S (96 °C/98 °C, signal 1, endothermic), melting of monoclinic S (110 °C/113 °C/114 °C, signal 2, endothermic) and the formation of polymeric chains of S (153 °C/154 °C, signal 3, endothermic). All measurements show an endothermic signal (4) between 340 and 425 °C which represents the melting with dissolution of Te in S. This signal shifts to higher T with decreasing content of S and for the sample with the lowest amount of S it is close to the melting point of pure Te in the literature (450 °C).^[23] The absence of an exothermic signal further confirms that the signal (350 °C, H4, exothermic) in Figure 1b is for the redox reaction of CdTe and S and not for the formation of the transport species, which is again not visible in these measurements. The details of the measurements can be seen in Table S3.

Table 1. Peaks in the DSC measurement of the closed system.

No.	T (S)/°C	T (CdTe)/°C	T (CdTe + S)/°C	Event	T/°C literature
1	96	–	–	S phase transition (rhombic to monoclinic)	95.28 ²²
2	111	–	108	Melting of monoclinic S	119.75 ²⁴
3	158	–	152	Formation of polymeric S	159 ^{24,25}
4	–	321	321	Melting of Cd	321 ²³
5	–	–	350	Formation of CdS and Te	–
6	–	445	–	Melting of Te	450 ²³

Table 2. Peaks of the DSC of CdTe and S with 2 heating and cooling cycles.

No.	T (first run)/°C	T (second run)/°C	Event	T/°C literature
H1	108	102	Melting of monoclinic S	119.75 ²⁴
H2	152	–	Formation of polymeric S	159 ^{24,25}
H3	–	342	Melting with dissolution of Te in S	–
H4	350	–	Formation of CdS and Te	–
C1	340	340	Solidification of Te + S	–
C2	75	75	Solidification of S	–

Transport Reaction of Te with S

First, the transport reaction of tellurium with sulfur was investigated for a closed system as shown in Figure 2a, where a proper chemical equilibrium can be achieved after a certain amount of time, applying wide thermodynamic control of the reactions. The source is in this case the side with higher temperature where Te formed by the redox reaction (Equation (3)) reacts with sulfur to form gaseous mixed Te–S-species according to Equations (2) and (3). The latter are subsequently transported to the sink side by diffusion, where they reform the elements until the equilibrium is reached. Sulfur is volatile and moved back to the source whereas purified Te is deposited at the sink. The results of the CVT in a closed system are listed in detail in the SI, Table S3. About 500 mg CdTe (2 mmol) were used as starting amount for each experiment in the closed system for a transport time of 72 h together with two equivalents of sulfur (150 mg) per tellurium, so that the pressure inside the ampoule would settle around 0.75 bar. An exact calculation of the pressure inside the closed system is challenging because of the different sulfur species present in the gas phase.^[27] The pressure was calculated with the ideal gas equation and with the simplification that only S₆ molecules are present in the gas phase.

In contrast, in an open system, as shown in Figure 2b the transport agent sulfur can leave the system at the end of the tube behind the sink, and therefore a chemical equilibrium cannot be fully reached. Due to exchange of material with the outside, such a system is not under thermodynamic control and applies other influences on the equilibrium. Thereby, adding further sulfur to the reaction is possible via an inlet at the source side the transport tube. This enables reuse of the chemicals used for the transport by moving the sulfur leaving the tube back to its beginning, strongly increasing the sustainability of the presented process.

For the respective experiments, the temperatures T_{source} and T_{sink} were selected similar to the ones in the closed system, while the amount of sulfur was increased up to tenfold to 1.5 g, since it can leave the end of the tube. It was mixed with 250 mg (1 mmol) CdTe and placed at the source in order to get quantitative results for the transport parameters based on the amounts of substances used, sulfur was not replaced continuously in these experiments. Argon was used as a carrier gas to move the gaseous species through the tube with a volumetric flow rate of 0.25 to 1.0 Lh⁻¹ in the tube (inner diameter: 14.5 mm, inner cross-sectional area: 1.65 cm²). The distance for the transport in these experiments was within a range of 5–

30 cm. The flow rate was low to offer a certain contact time for reaction to sulfur inside the oven as long as possible. After all sulfur left the transport tube, the CVT came to a halt reducing the reaction time to a maximum of 4 h. A higher flow rate might support a faster transport in the open system if the amount of sulfur is not a limitation. Otherwise a higher transport rate would only lead to the sulfur being removed faster from the tube, stopping the CVT even earlier. Therefore the influence of the flow rate was not investigated any further. The results of the CVT in flow tubes are given in detail in the SI, Table S2.

Both setups were analysed for the same transport reaction, starting with CdTe and S at the source and using sulfur as oxidizing and transport agent for Te. The results of thermal analysis provided information that the redox reaction for the formation of CdS and elemental Te, Equation (1), happens at 350 °C and is therefore considered as minimum temperature at the source side. The maximum temperature was set at 444 °C, the boiling point of S, as the vapour pressure of Te, 2.3710⁻⁴ atm,^[28] is still low enough to avoid sublimation of Te, which would lead to smearing out of Te from the source side. The temperature of the sink typically differs by 50–100 °C to reach a significant change in the chemical equilibrium to promote the back reaction. The transported Te was then checked for impurities and weighed to calculate the yield and the transport rate for different temperatures at source and sink.

The yield of a transport reaction is determined by the weight of the product at the sink and the total mass of Te in the ampoule (Equation 4).

$$\text{yield} = \frac{m(\text{Te at sink})}{m(\text{Te in ampoule})} \cdot 100\% \quad (4)$$

According to the acquired data which is presented as a heat map (Figure 3a) an increase of T_{source} generally causes a rise of the yield of Te due to a higher reaction rate and faster diffusion.

A T_{source} of 400 °C is sufficient for an almost complete transport of Te (97.8%) for $T_{\text{sink}}=300\text{--}350\text{ }^{\circ}\text{C}$ for the closed system, which is in this case up to 300 mg in 72 h. Increasing T_{sink} from 325 to 350 °C leads to similar transport rates and yields. However, increasing T_{sink} beyond 350 °C leads to a decrease of the yield because a smaller temperature gradient results in a lower diffusion rate. A likewise increase of T_{source} enables high yields also at higher T_{sink} but for reasons of sustainability, such as energy saving, it is also evident to determine low temperature borders of an efficient transport. Accordingly, a transport at 400 °C T_{source} and 300 °C T_{sink} would

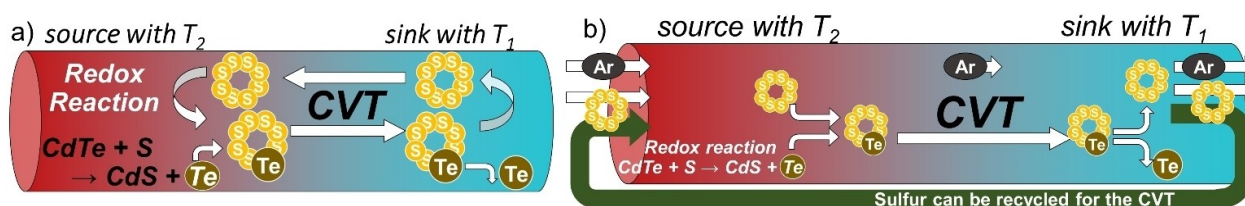


Figure 2. a) Schematic depiction of CVT of Te with S in a closed system. b) Schematic depiction of CVT of Te with S in an open flow system.

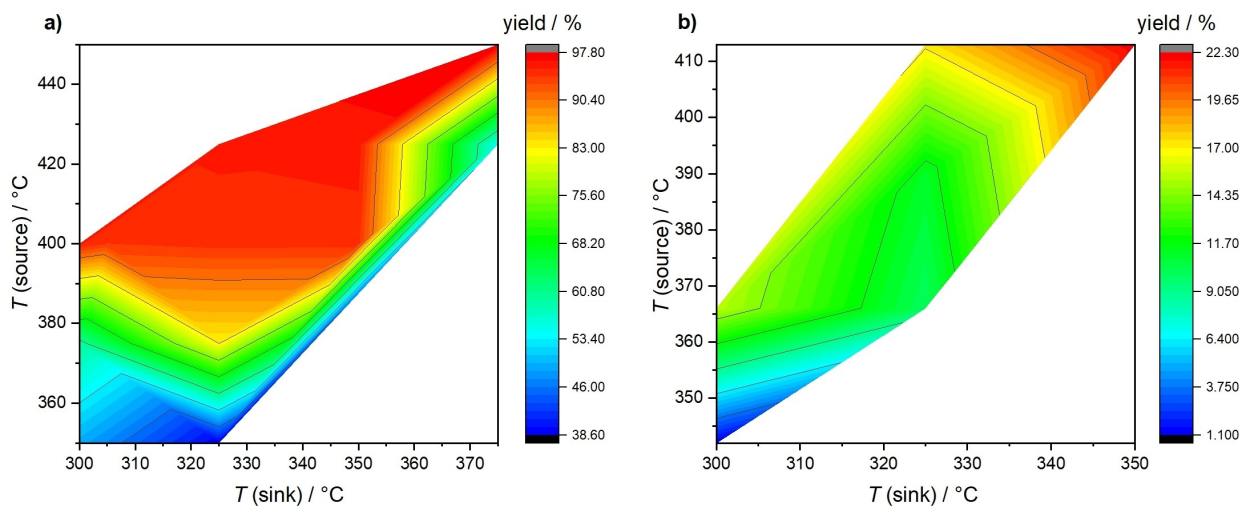


Figure 3. a) Heat map with the yield of Te depending on T_{source} and T_{sink} of the closed system; starting with 561 mg CdTe, a yield of 100% equals 198.6 mg Te, b) heat map for the open system for identical temperature parameters, starting with 240 mg CdTe, a yield of 100% equals 127.6 mg Te.

be the best choice. Extended grinding had no significant effect, because yield and transport rate were already quite high.

In the open flow tube system, the yield is also increasing with increasing T_{source} . In contrast to the closed system, the yield of the open system with the setup for 4 h (OS1–OS08) is considerably lower with 22.3%, which equals 28.4 mg. As expected, this is the result of the fixed amount of sulfur and its limited contact time to tellurium in the argon stream, also limiting the time the transport was running. Although looking non-favourable at first, this is achieved in 1/18 of the reaction time in the closed system, so that moving sulfur around in cycles leads to a preferable process in an open system that is about four times faster than a process in a discontinuous closed system. The influence of T_{sink} is reduced, as the open system provides a continuous gradient to room temperature in the flow tube.

Another important parameter of a transport reaction is the temperature difference between source and sink. Figure 4 gives the yield of Te for different temperature gradients in dependence of T_{source} for closed (a) and for open system (b). A higher gradient is generally beneficial for the yield because it promotes the diffusion. 25 °C seems to be too low because the yield is below 40%. In the closed system, for temperature gradients of 50, 75 and 100 °C, yields close to 100% are observed at 400 °C for T_{source} . Gradients of 75 and 100 °C have similar yields also at higher T_{source} because T_{sink} of 375 °C already makes the back reaction of Equations (1) and (2) for the formation of elemental Te thermodynamically unfavourable. This should also be the case for other temperature gradients once the T_{sink} reaches 375 °C. For the open system there is no such trend noticeable (Figure 4b) and rate of the back reaction as well as the diffusion

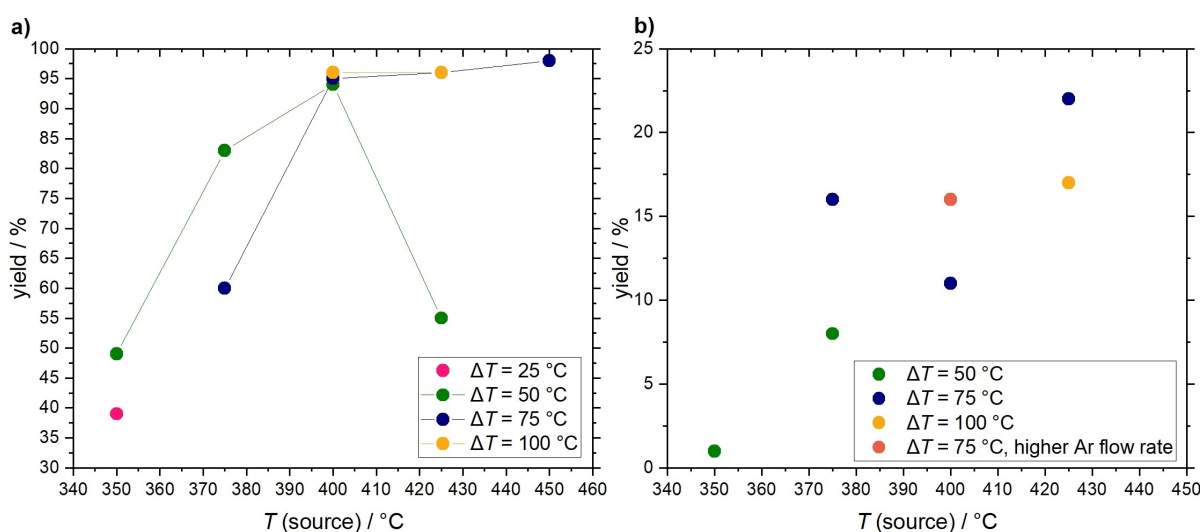


Figure 4. a) Yield of Te at the sink of the experiments in the closed system for different temperature gradients depending on T_{source} . Starting with 561 mg CdTe, a yield of 100% equals 198.6 mg Te, b) yield of Te at the sink of the open system for different temperature gradients in dependence of T_{source} . Starting with 240 mg CdTe, a yield of 100% equals 127.6 mg Te.

of sulfur from the sink to source are less important for the result of the transport because of the continuous flow.

To further quantify the transport processes, also transport rates were determined. The transport rate gives the average mass which is transported in one hour for a CVT and is therefore a crucial parameter for an effective transport.

$$\text{transport rate} = \frac{m(\text{Te at sink})}{\text{duration of transport}} \quad (5)$$

The transport rates are presented in Figure 5 for the closed (a) and the open (b) system. For the closed system, the transport rate increases in general with higher T_{source} and reaches a maximum at around 4 mg h^{-1} for experiments with T_{source} of 400°C . The transport rates for the open system are surpassing the ones for the closed system in most instances reaching a maximum of 7.1 mg h^{-1} for T_{source} of 425°C . A higher T_{source} leads to a higher transport rate. The overall relations of the transport rates are similar to the relations of the yield, because they were all determined for the same time which was 72 h for the closed and 4 h for the open system.

Perfectly concentric alignment of the flow tube in the center of the oven tube (OS09) resulted in a considerably higher yield of $65.6 \text{ mg}/51\%$ as well as a higher transport rate, 21.9 mg h^{-1} . This indicates that the homogeneity of the temperature field influences the rate of transport as well. This increase renders the open transport even more favourable for a recovery process..

Purity of Products

Since this CVT is supposed to be used for potential recycling of Te, the purity of the transported product is a crucial parameter. Therefore the products of the CVT were analysed for their purity

with various methods for different trace elements and mutual confirmation.

First, PXRD was used to identify phases in the products at the source and the sink of the transport reaction. All powder diffractograms are presented in die SI, and the products at the sink of the closed system (Figure S1, S2 and S3) as well as of the open system (Figure S7) show only reflections of Te. Impurities can still be present in a sample and do not appear in a powder diffractogram if their amount is below 1–5%, depending on crystallinity and scattering ability. Therefore, PXRD only enables a quick but rough qualitative insight into the purity of a sample with respect to the detection limit for impurities. In Figure S4, S5 and S6 the diffractograms of the materials at the source of the closed system are depicted. All diffractograms show CdS as main phase, but all samples with $T_{\text{source}} < 400^\circ\text{C}$ also show Te and/or CdTe as impurities indicating an incomplete transport and in case of CdTe also an incomplete redox reaction, corroborating the findings of the yield determinations. Te is also present in all samples for a temperature gradient $\leq 50^\circ\text{C}$ with the exception of $T_{\text{source}} = 400^\circ\text{C}$ and $T_{\text{sink}} = 350^\circ\text{C}$, which shows no impurities at source. Interestingly, the transport with the same ΔT but higher temperatures as well as for lower temperatures have Te left at the source side, indicating that $T_{\text{source}} = 400^\circ\text{C}$ and $T_{\text{sink}} = 350^\circ\text{C}$ are the optimal temperatures for the CVT with the lowest reasonable altogether temperature. The powder patterns for the sink of the flow tube experiments (Figure S7) show only reflections for Te. The respective patterns for the source (Figure S8) show reflections for CdS as well as Te in all of them and for some also CdTe corroborating the lower yield requiring several recovery cycles.

In contrast to the closed system, the presence of unreacted CdTe in the open system follows no trend. For the open system with a concentric flow tube the PXRD pattern of the transported product (Figure S10) showed only reflections of Te and two very low intensity reflections of SiO_2 being the material from the flow tube. The PXRD pattern of the source (Figure S9) showed

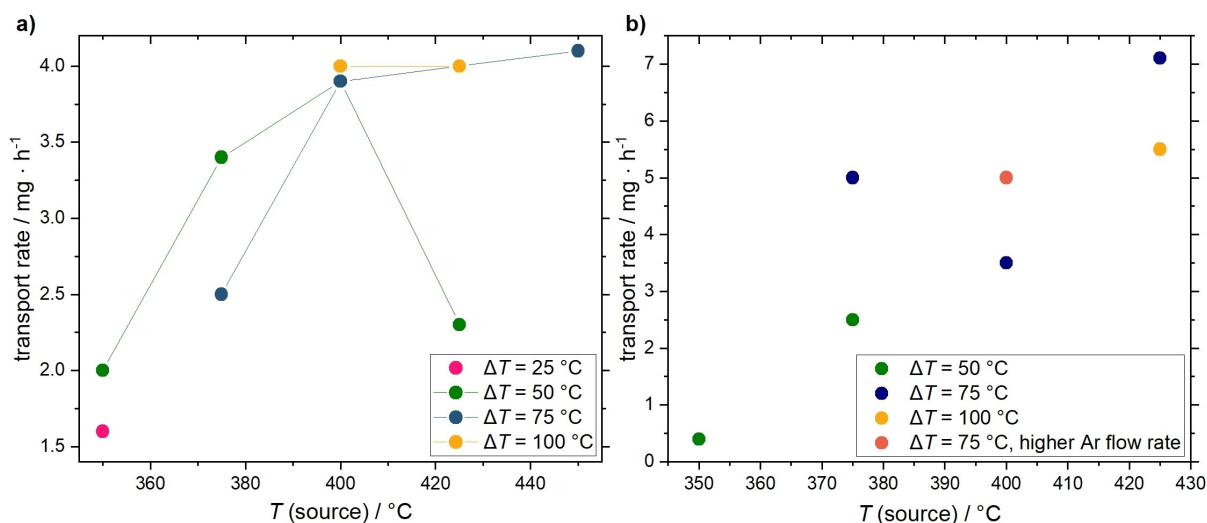


Figure 5. a) Transport rate of Te in the closed system for different temperature gradients depending on T_{source} : The starting amount of CdTe was 561 mg. b) transport rate of Te for open systems for different temperature gradients in dependence of T_{source} . The starting amount of CdTe was 240 mg.

only reflections for CdS and also for Te that was not transported.

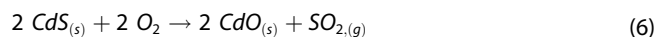
MP-AES is an appropriate method to check for trace amounts due to its low limit of quantification (LOQ) of 0.05 wt%, e.g. of Cd in the transported Te. The products at the sink of the closed system as well as of the open system were analysed by MP-AES, but no Cd could be detected above the LOQ, indicating that no traceable CVT involving Cd or sublimation of Cd takes place. This is reasonable because Cd has a different electronic structure as Te and S therefore the formation of transportactive species with S is unlikely and the boiling point is with 765 °C quite high.^[29] This is also consonant with the results of SEM-EDX investigations, which have a lower detection limit, about 0.2 wt%, compared to PXRD but can overinterpret light elements. However, SEM-EDX is sensitive to the surface with an unknown information depth typically < 1 µm due to the relatively low acceleration voltage of 8 keV used in our case and for the heavy element Te. Several conditions for the closed (Figure 6 and Figures S14 and S15) and open system (Figure S17–S20) were also checked with SEM-EDX for the purity. The Tellurium content was always above 99 wt% and a small amount of S between 0.2 and 0.6 wt% was detected. Cd was not detected at all, confirming the results of the MP-AES. One sample of the closed system is shown in Figure 6 with an SEM-image of the particle (a) and the SEM-EDX-mapping of Te and S (b), indicating traces of S for the transported Te.

Recovery of Cd

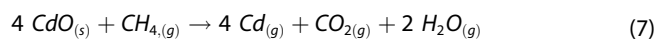
As shown, cadmium is not taking part in the CVT and hence is staying at the source. This is advantageous for its recovery,

which is important too, due to its toxicity, hazard for the environment and scarcity.^[30] Therefore it is worth to separate also cadmium for making it reusable and avoid special waste while cleaning the rest of the recyclable material of it at the same time.

Here fore, the relatively low boiling point of elemental Cd (765 °C) is beneficial for a separation via the gas phase.^[29] After the CVT of Te, the Cd is present as CdS. Accordingly, be oxidised with oxygen to CdO at elevated temperatures in a roasting process, which can be done under normal atmosphere according to Equation 6.



Subsequently, CdO was reduced in a gas stream of methane at elevated temperatures which simultaneously causes the evaporation of Cd so it could condense at the colder spot of the tube for separation, as described by Equation 7.



Formation of CdO and Recovery of Cd by Reduction with Methane

To get a better understanding of the oxidation process of CdS and to find the most suitable temperature for it, CdS was also analysed with DTA/TG coupled with mass spectrometry under dynamic flow of synthetic air until 1200 °C (Figure 7a). The reaction of CdS with O₂ starts at 685 °C, indicated by a mass increase of 5% and the formation of a ternary phase of the

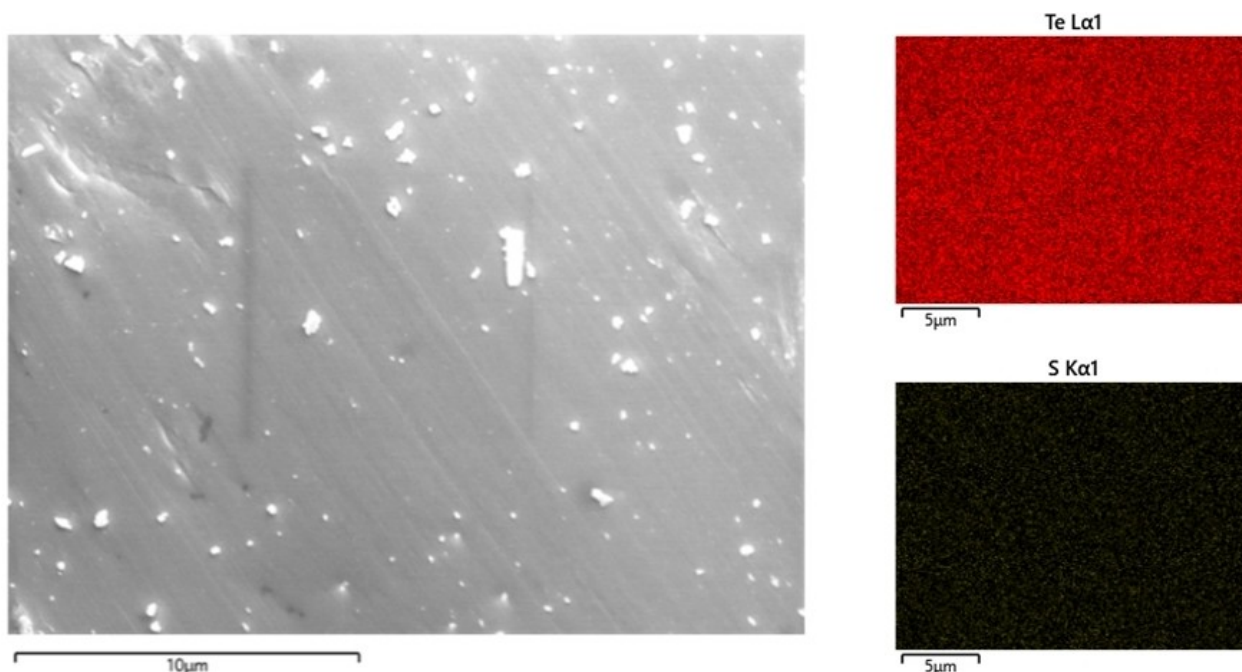


Figure 6. a) Scanning Electron Microscopy image of the sink material after the transport reaction in a closed ampoule from 375 °C to 325 °C. b) EDS map of Te and S.

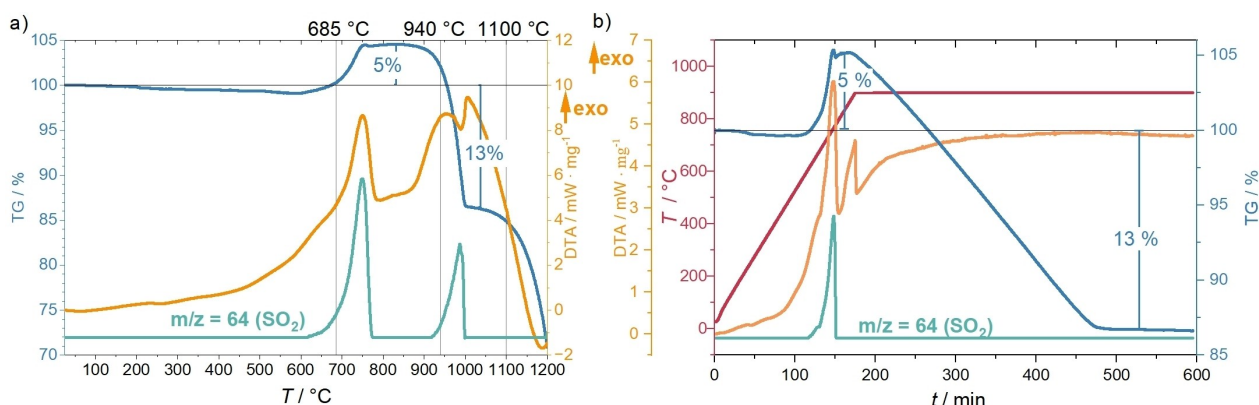


Figure 7. a) Simultaneous DTA/TG coupled with mass spectrometry of the reaction of CdS and air until 1200 °C with mass spectrometric detection of SO₂ ($m/z=64$). b) Simultaneous DTA/TG coupled with mass spectrometry of the reaction of CdS and air heated to 900 °C and holding the temperature for ten hours, with mass spectrometric detection of SO₂ ($m/z=64$).

composition (CdS_xO_y). The process can neither just be attributed to the formation of CdO or CdSO₄, as the mass increase related to its formation had to be significantly higher of about 44% and formation of CdO reduces the remaining mass. In addition, release of SO₂ is visible in the mass spectrum.

At around 940 °C a mass decrease of 13% in total indicates the formation of CdO (theoretical mass loss is 11%). Another mass decrease starts at 1100 °C together with an endothermic signal in the DTA and does not finish until the end of the measurement at 1200 °C, which marks the evaporation of CdO. This was confirmed with an additional DTA/TG measurement of pure CdO that shows a similar mass decrease combined with an endothermic signal (Figure S25). After the DTA/TG measurement of the reaction of CdS with O₂, PXRD of the remaining material confirms the complete oxidation of the CdS by showing only reflections for CdO (Figure S11).

To get further insights in the reaction at around 700 °C, a small amount of CdS was heated in a muffle oven open to the atmosphere to 700 °C for 17 h and 650 °C for 65 h respectively. The diffractograms of the products (Figure S12) showed a complex mixing of phases, mainly reflections for Cd₃OSO₄ and minor reflections for CdO and CdSO₄. Therefore heating CdS at the lowest reaction temperature of CdS and O₂ will not lead to the formation of pure CdO, making higher temperatures necessary for a complete formation of CdO.

Another simultaneous DTA/TG measurement coupled with mass spectrometry (Figure 7b) of CdS was done to determine the lowest temperature for complete formation of CdO and the time that is required for the process. After 130 min at 740 °C the formation of the oxysulfide mixture starts indicated by a mass increase and an exothermic reaction signal, while a first release of SO₂ is observed. This process is followed by the formation of CdO, recognisable by the decrease in mass, which ends after 5 h holding the temperature at 900 °C accompanied by a mass loss of 13%, indicating a complete oxidation of CdS (calc. 11%). Formation of CdO was subsequently confirmed by PXRD (Figure S13).

The practical implementation to obtain the elemental Cd and separation from other remaining components of a potential

solar cell was done by a combined reduction and distillation step in a flow tube consisting of quartz glass to withstand high temperatures. Methane gas was used as an abundant reducing agent for the reduction of CdO (Equation (7)). A typical mixture of materials used for CdTe solar cells consisting of SnO₂, In₂O₃ and the already oxidised CdO, was heated in a methane gas stream at 750 °C for 2 h. After the reaction, only metallic Cd, (PXRD shown in Figure 8b), condenses at the inside of the

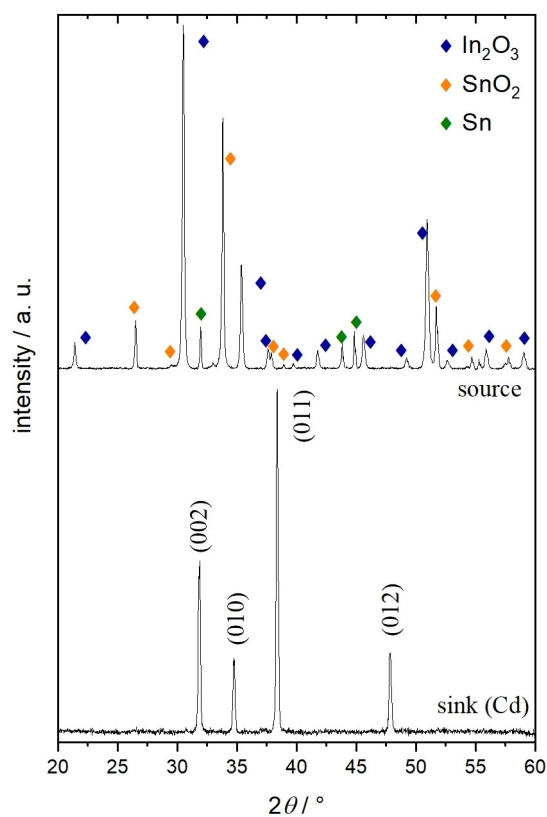


Figure 8. a) PXRD of source after the reduction of CdO in methane gas stream, b) PXRD of Cd reduced and sublimated in methane gas stream.

quartz tube at the end of the oven tube, where the temperature was below 600 °C.

At the source In_2O_3 , SnO_2 and elemental Sn were determined with PXRD but no Cd, (Figure 8a), implying that for CdO, both reduction and evaporation are complete and also SnO_2 is partly reduced (equation 8) but the formed Sn did not evaporate. Accordingly, the process is also suitable in the presence of other relevant components of a potential solar cell.



Conclusions

In the current study, a combinatorial chemical recovery process of the critical resources Te and Cd from CdTe was developed with the all-abundant chemicals sulfur, air and methane. For recovery of Te, moderate temperatures below 500 °C can be applied. Key component is the chemical vapor transport (CVT) of Te with S giving mixed species of Te–S sulfur rings. Conditions heading for an efficient transport at the lowest possible temperatures were investigated for a closed system as well as for an open flow system. Sulfur as transport agent already functions below its actual boiling point and also as oxidizing agent to form elemental Te from CdTe. Accordingly, both reactions can be carried out simultaneously in one procedure, making this the first CVT of Te with S starting from CdTe, to the best of our knowledge. In the closed system a temperature of only 400 °C at the source proved sufficient for an optimal yield of 97.8% after 72 h. In the open system evaporation of sulfur requires 370 °C and slightly higher temperatures of 425 °C at the source combined with four to five cycles of moving the used sulfur in low gas stream around. Still, transport in an open system is about four times faster than in a closed, discontinuous system allowing for a recovery of about 50%/h. These conditions are way below the sublimation temperature of Te of 1000 °C and indicate a reduction of energy consumption for the proposed process compared to transporting elemental Te via the gas phase. The presented gas phase transport is also aligned with good purity already at the initial transport step. For example, no impurities of Cd in the deposited Te were detected above the limit of quantification of 0.05 wt% (0.057 at%) via MP-AES. S can be present in the sink as seen in SEM–EDX measurements up to 0.9 wt% but can preferably be removed in an open system with the ongoing gas stream.

Subsequent separation of Cd was achieved in two steps, an oxidation of CdS in air at 900 °C followed by a reduction of formed CdO with natural gas at 750 °C. The temperature used for the reduction was sufficient for a simultaneous distillation of Cd for a beneficial separation, e.g. from other photovoltaic components such as indium tin oxide (ITO), namely from SnO_2 and In_2O_3 .

The results presented in this study offer a new combinatorial pathway for sustainable recovery of the two toxic critical resources Te and Cd and thereby for a recycling from thin film CdTe solar cells. Strong advantages are low procedure temperatures for Te recovery and thereby lower energy consumption

compared to the lately presented vacuum distillation procedure. Further advantages lie in the use of all abundant chemicals only, as well as an overall low amount of chemicals required compared to the established processes like acid leaching and lower temperatures. Beneficially, excess S, air and methane can be directly re-used in a continuous flow procedure based on the open flow tube setup presented in this work. It can also be expected that the CVT in an open system allows for sufficient high transport rates when sulfur is brought continually into the system during the reaction. Therefore, this should be an applicable setup in an industrial application including cycling and re-use of excess sulfur, as such a CVT was already industrially implemented in the Mond process or the Van Arkel–de Boer process. For an environmentally friendly process, the generation of hazardous gaseous sulfur species, such as H_2S and SO_2 , need to be taken care of by appropriate known exhaust treatments. New catalytic methods might enable a reduction of SO_2 to S without the production of large amounts of waste, integrating this process further into a circular economy. Additionally, methane used for the reduction of CdO could potentially be produced from CO_2 and H_2O using excess electricity from renewable sources with the power-to-gas technology.

Experimental Section/Methods

Transport Reaction in Ampoules

For the CVT in a closed system 0.562 g (2.34 mmol) CdTe (Sigma Aldrich, > 99.98%) and 0.150 g (4.68 mmol) S (Merck, 99.5%) were loaded in quartz ampoules (200 mm length, diameter: 14.5 mm) which were then evacuated to 0.05 mbar. A three-zone-oven (Carbolite TZF 12/65/550) was used to apply the temperature gradient. The ampoules were placed so that the middle zone was the sink with the lower temperature and one of the zones on the outside was the source with the higher temperature. Therefore, two experiments could be run at the same time.

Transport-Reaction in a Flow Tube

The described three-zone-oven was also used for the transport in an open system utilising a quartz tube (length 900 mm and diameter 14.5 mm). The tube was connected with an Argon gas supply. The tube was purged by an Argon flow of 2 L h^{-1} for 30 min for inertisation and the flow was reduced to $0.25\text{--}1.0 \text{ L h}^{-1}$, when the heating process was initiated. The first zone of the oven was used as source side, where a ceramic boat was positioned containing the starting materials 0.240 g (1 mmol) CdTe and 1.500 g (46.79 mmol) S, the zone in the middle was used as sink for Te and the last zone was used as a sink for S.

Separation of Cd

A muffle oven (Nabertherm LE 6/11/R/) was used for the oxidation of CdS (abcr, 98%). 20 mg CdS (138.48 mmol) were heated open to the atmosphere at 900 °C for 14 h in a ceramic crucible and cooled down by switching off the oven. The separation of Cd was realized by simultaneous reduction of CdO (abcr, 99.999%), with SnO_2 (reagent grade) and In_2O_3 (Alfa Aesar, 99.95%) in a natural gas

(mainly methane) stream, flow rate 0.25 L h^{-1} , and sublimation at 750°C with a duration of 2 h.

Powder Diffractometry

X-ray powder diffraction patterns were recorded with the X'Pert Pro (PANalytical) containing an Empyrean Cu LFF X-ray tube at 40 kV and 40 mA and an X'Celerator detector. A 0.04 rad Soller slit, a 10 mm beam mask, an anti-scatter slit of 1° and a divergence slit of 1° were installed for the incident beam path. Within the diffracted beam path an anti-scatter slit of 0.5° , a 0.04 rad Soller slit and a Nickel Beta-filter (0.02 mm) were placed. The samples were placed on a sample holder with a silicon waver and flattened using a spatula. The diffraction pattern was recorded from 20 – 60 in 2θ with a step size of 0.0167° by using monochromatic Cu-K α radiation ($\lambda = 150.46 \text{ pm}$).

Thermal Analysis

Simultaneous Differential Thermal Analysis and Thermogravimetric Analysis (STA) of S, CdS and CdO were carried out on a NETZSCH STA-409-PC instrument coupled with NETZSCH QMS (Quadrupole-Mass Spectrometer) 403 flow of 50 ml min^{-1} (for S) or in a mixture of the argon (20 ml min^{-1}) and synthetic air (30 ml min^{-1} , for CdS) with a heating rate of 5 K min^{-1} in the temperature range from 25 to 400°C . The samples were measured in Al_2O_3 crucibles. A sample carrier with a thermocouple type S was used, and temperature and sensitivity calibration was carried out with materials: In, Sn, Bi, Zn, Al, Ag, and Au. The mass of the sulfur sample (Figure S26) was 31 mg (0.97 mmol). The mass of the CdS sample was 20.3 mg (0.141 mmol) (Figure 7a) and 48.7 mg (0.337 mmol) (Figure 7b). The mass of the CdO (Figure S25) sample was 3.9 mg (0.30 mmol).

Differential Scanning Calorimetry (DSC) analysis of CdTe, S, CdTe + S and Te + S were carried out using a NETZSCH STA-404-C instrument in an argon flow of 150 ml min^{-1} with a heating rate of 5 K min^{-1} in the temperature range from 20°C to 500°C (two heating and two cooling cycles were recorded). Quartz ampoules (outer diameter 6 mm, wall thickness 1 mm, height 10–15 mm) with a polished bottom were used for the measurements. Samples were placed in these ampoules that were later fixed in a quick-fit and vacuumed. During ampoules' sealing, the sample containing part was periodically cooled with liquid nitrogen and held with cooled metal tweezers. A sample carrier with a thermocouple type E was used, and temperature and sensitivity calibration was carried out with materials: In, Bi, Pb, Zn, and Al. The sample amounts for the measurement (Figure 1) were 9.9 mg (0.31 mmol) S for pure sulfur, 9.1 mg (0.038 mmol) CdTe for pure CdTe, and 9.1 mg (0.024 mmol) CdTe and 5.8 mg (0.18 mmol) S for the combined measurement. The combined mass for the measurement with two cycles of CdTe and S was 13.1 mg (Figure 1b). The combined mass of the measurements with different Te:S ratios (Figure S27 and Figure S28) were 11.1 mg for Te:S = 1:2, 10.9 mg for Te:S = 1:1, 10.2 mg for Te:S = 1:0.25 and 10.9 mg for Te:S = 1:0.06.

SEM-EDX

Scanning electron micrographs were created using a Merlin Gemini (Zeiss) with an acceleration voltage of 3 kV, a current of 100 pA and a working distance of 5 mm. Recording of energy dispersive X-ray spectral mappings was done with an XMAX-50 detector (Oxford Instruments) applying a working distance of 5.5 mm, a current of 1 nA and an acceleration voltage of 8 kV. Samples were dripped onto sticky carbon pads which were attached to the specimen

holders before. Any excess of sample was removed carefully by using pressurized air blown from above the specimen holders.

MP-AES

The concentration of Cd^{2+} was determined by microwave assisted atomic emission spectrometry (MP-AES) with the principle of standard addition using a MP-AES 4210 instrument from Agilent Technologies. Solutions with a concentration of 100 mg L^{-1} in HNO_3 with $c \sim 1\%$ were produced. The sample solutions were spiked with different concentrations of Cd^{2+} from 0.05 mg L^{-1} to 5 mg L^{-1} (0.1 mg L^{-1} , 0.5 mg L^{-1} in, 1 mg L^{-1}) to rule out effects of the matrix on the measurement. A $\text{Cd}(\text{NO}_3)_2$ standard solution ($c = 1000 \text{ mg L}^{-1}$) Supelco® from Sigma Aldrich was used. The samples were analysed with an MP-AES 4210 instrument from Agilent Technologies. The emission of the wavelength from Cd with 228.802 nm was evaluated.

Supporting Information Summary

The Supporting Information contains tables of transport experiments' parameters and results, powder X-ray diffraction plots and additional SEM images with EDX spectra of the product after transport reactions, MP-AES results and calibration curves, additional thermal analysis table and plots, and a photograph of the distilled Cd in the quartz tube.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

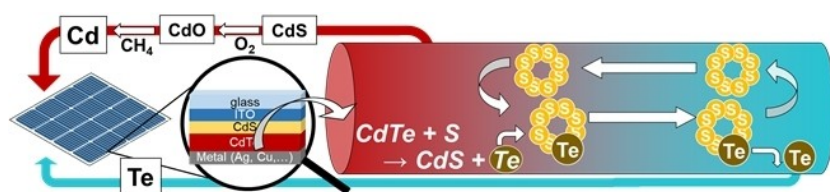
Keywords: Cadmium telluride · Chemical vapor transport · Critical resources · Recycling · Solar cells

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RESEARCH ARTICLE



Recovery of the two critical elements Cd and Te from CdTe for recycling of solar cells was tested using chemical vapour transport of Te with S as transport agent at temperatures

below the boiling point of S. Cd is also recovered via the gas phase by oxidation of CdS and reduction with methane.

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1 – 13

Combinatorial Separation of Cd and Te from CdTe via Chemical Vapour Transport with Sulfur and Air/Methane Treatment for the Recovery of Critical Resources from Thin Film Solar Cells

