



A new synthetic route for the preparation of metal tellurides

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ARTICLE INFO

Article history:

Received 11 April 2013

Accepted 4 October 2013

Available online 11 October 2013

Keywords:

Cadmium telluride

Mercury telluride

Synthesis

Bis(diphenylphosphino)amine

ABSTRACT

A new method of synthesis for the formation of metal tellurides of the type MTe (M = Cd, Hg) is reported. The compounds were prepared by the reaction of cadmium carbonate (or mercury oxide, respectively) with tellurium and bis(diphenylphosphino)amine in toluene at 160 °C. The products were characterized by powder XRD and EDX analyses. The whole chemical process is discussed.

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Metal tellurides form a wide group of compounds with promising applications mainly in optical devices, such as solar cells, but also in thermoelectrical devices and others [1,2]. Thus many methods of synthesis of these materials were developed. The classical approach to obtain metal tellurides is based on the heating of the corresponding metal with elemental tellurium at high temperatures or precipitation reactions between metal salts and sodium telluride [3].

Many different synthetic routes have later been successfully used to produce metal tellurides. Electrochemical reactions involve reduction of tellurium cathode by passing electrical current [4,5]. Another method is mechanical alloying, consisting in milling of powdered elements under appropriate conditions [6]. Direct reaction between elements under ambient conditions in *n*-butylamine leads to preparation of several metal tellurides [7]. Solid state metathesis reactions can also be used to prepare metal tellurides, using alkali metal telluride and (commonly) metal halide as starting materials [8,9].

In last decades, interest in metal telluride synthesis, connecting with progress of nanoscience, is focused on their nanoscopic form. Broad chemical variability is kept in the syntheses, let us mention only two examples, which are crucial for our research. The first method is solvothermal reaction between Me₂Cd and trioctylphosphinetelluride (TOPTe), where cadmium telluride is formed [10]. Many modifications of solvothermal processes have been developed to prepare different metal tellurides using various starting materials, capping agents and reaction conditions [11]. The second approach to obtain metal tellurides

is decomposition of single-source precursors (SSPs). These are usually coordination compounds containing both metal and tellurium with a pre-built chemical bond between them. Decomposition of the precursor under appropriate conditions leads to a well defined material. In contrast to metal sulphides and selenides, synthesis of suitable SSPs for synthesis of metal tellurides is much more difficult, because tellurium-containing ligands are usually less stable than their thio- and seleno-analogues [2]. This makes their synthesis problematic or even impossible. However, it is possible to use tellurolates, such as HTeSi(SiMe₃)₃, to prepare an appropriate metal complex and metal telluride in the next step [12,13]. A more suitable way seems to be via complexes of ditelluroimidodiphosphinates. The ditelluroimidodiphosphinate ligand itself was first published in 2002 [14] and the appropriate complexes M[(TePⁱPr)₂N]₂ (M = Cd, Hg) were showed to be suitable for preparing MTe [15,16].

The two mentioned methods, that are widely used, have several advantages and disadvantages. The most important disadvantage of the solvothermal processes, working with extremely toxic materials (such as Me₂Cd and H₂Te), was eliminated using the SSPs method. However, a few more synthetic steps have been added, because the ligand and also the precursor itself must be synthesized, isolated and purified before metal telluride can be finally prepared.

In this communication we present a method eliminating both of the disadvantages mentioned above. We introduce a direct preparation of metal tellurides in one reaction step using less hazardous chemicals and temperatures much below 200 °C.

In a typical synthesis, Ph₂PNHPPH₂ (200 mg, 0.52 mmol; prepared according to the literature method [17]), Te (33 mg, 0.26 mmol), and metal source (CdCO₃: 45 mg, 0.26 mmol or HgO: 56 mg, 0.26 mmol, respectively) were suspended in toluene in a Parr autoclave. The autoclave was then filled with argon, closed and heated at various

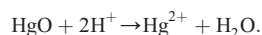
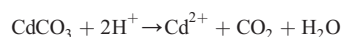
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temperatures (60–180 °C, see below) for about 20 h. The resulting black powder was collected by filtration, washed with toluene and dried under laboratory conditions. Typical yield of the synthesis varies from 95% to 99%.

The Parr autoclave is a Parr Acid Digestion Vessel 4749 with the inner cuvette volume of 23 ml. Powder XRD data were collected on a Stoe-Cie STADI-P diffractometer operating in transmission mode (CoK α_1 radiation ($\lambda = 1.788965$ Å); linear PSD detector; curved Ge(111) monochromator; scanning range 8–75° 2 θ ; step size 0.010° 2 θ ; counting time of 5 s). SEM images were acquired on a TESCAN MIRA3 XMU scanning electron microscope equipped with Schottky field emission gun (FEG). A Bruker XFlash 6|60 detector (60 mm² SDD) was used to perform EDX analysis; results were evaluated using an Esprit 1.9 software.

The chemical behaviour of the process will be discussed in the following paragraphs. The hydrogen atom of the –NH– group of Ph₂PNHPPH₂ is slightly acidic and this means that it can react with a suitable base, in our case with cadmium carbonate or mercury oxide:



By such protolysis, M(2+) ions (M = Cd or Hg) are released from insoluble cadmium carbonate or mercury oxide in our system.

Phosphorus(III) atoms in Ph₂PNHPPH₂ seem to be responsible for the reduction of tellurium to telluride, forming very probably an unstable P–Te species, which reacts with M(2+) ions to give a precipitate of metal telluride. It was described, that the reactivity of neutral Ph₂PNHPPH₂ towards tellurium, that is considered to be negligible, increases with deprotonation of Ph₂PNHPPH₂ [14].

The overall “equation” of the described process with cadmium carbonate used as starting material might be:



We confirmed the formation of cadmium telluride and mercury telluride by powder XRD analysis (see below), however we were not able to identify all by-products of this reaction. One of them might be Ph₂P–N=P(Ph₂)–O–P(Ph₂)=N–PPh₂, which seems to decompose after the reaction forming a mixture of different products. A compound similar to Ph₂P–N=P(Ph₂)–O–P(Ph₂)=N–PPh₂ was earlier reported in literature [18].

The presence of acidic hydrogen in Ph₂PNHPPH₂ molecule is crucial for the system studied. Using a similar ligand that does not contain acidic hydrogens, e.g., 1,4-bis(diphenylphosphino)butane, the reaction does not lead to the formation of metal telluride. In X-ray powder diffraction pattern obtained on the sample after the reaction, only diffraction lines belonging to starting materials are observed.

The molar ratio of reactants was chosen in agreement with the overall equation to 2 Ph₂PNHPPH₂: 1 Te: 1 CdCO₃ (or HgO, respectively). It is clear, that to obtain pure product, the ratio between Te and CdCO₃ (HgO) must be 1:1. The decomposition of each carbonate (oxide) requires 2 protons, so the final ratio is 2:1:1.

In attempting to prepare cadmium telluride we conducted a series of reactions under different temperatures, from 60 °C to 180 °C, while other conditions were constant. X-ray powder diffraction patterns (Fig. 1) of products of selected reactions show, that cadmium telluride is already formed at 130 °C, but is not pure yet (see Fig. 1, some of the sharp diffraction lines at 14–33° 2 θ belong to the starting materials). Starting at 160 °C, only peaks belonging to cadmium telluride can be seen in X-ray powder diffraction pattern of the product.

As mentioned, we conducted also reactions with mercury oxide in order to prepare mercury telluride. The powder XRD analysis confirmed

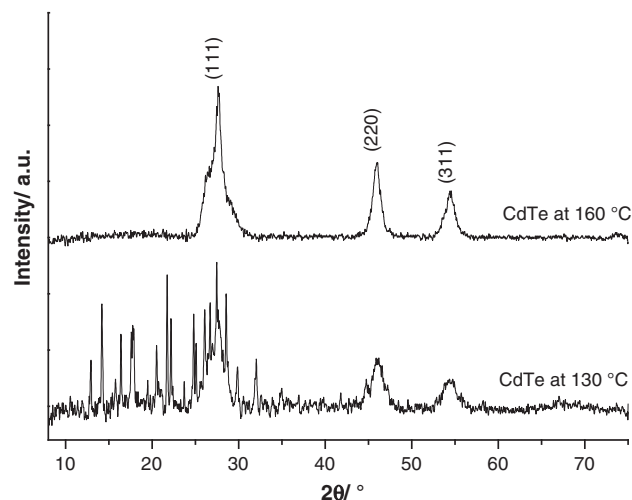


Fig. 1. X-ray powder diffraction patterns of CdTe prepared at 130 °C (bottom) and 160 °C (top) (PDF No. 015-0770).

the formation of mercury telluride (Fig. 2). In contrast to cadmium telluride, we obtained pure mercury telluride at the reaction temperature of 150 °C, while other conditions, such as reaction time and solvent, were identical.

Purity of prepared CdTe and HgTe was verified by EDX analysis. We found following average contents of elements in our products: CdTe: Cd found 47.59% (calc. 46.84%), Te 50.17% (53.16%), O 1.69% and Cl 0.55%. HgTe: Hg found 60.71% (calc. 61.12%), Te 37.27% (38.88%), C 0.94%, N 0.61% and O 0.47%. Both products are free of phosphorus; HgTe contains a small amount of carbon (<1%), possibly coming from the carbon tape. The presence of N and O in the samples could be explained by adsorption of these gases on the surface of the particles and in the case of oxygen also by partial surface oxidation of the tellurides as the samples were stored on air for several months. Traces of chlorine were confirmed only in several samples of CdTe, the amount of Cl seems to be very close to the detection limit of the detector used. By our opinion chlorine originates from CdCO₃.

Fig. 3 shows a SEM image of prepared CdTe. CdTe particles have spherical or almost spherical shape. Unfortunately the particle size distribution is broad. We can see particles with diameter in order of

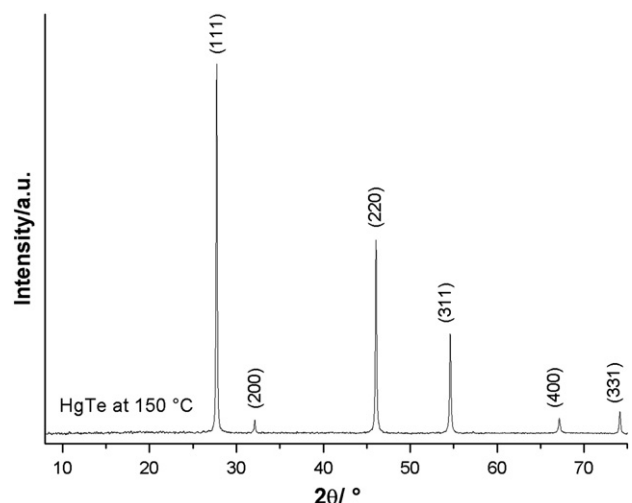


Fig. 2. X-ray powder diffraction pattern of HgTe prepared at 150 °C (PDF No. 032-665).

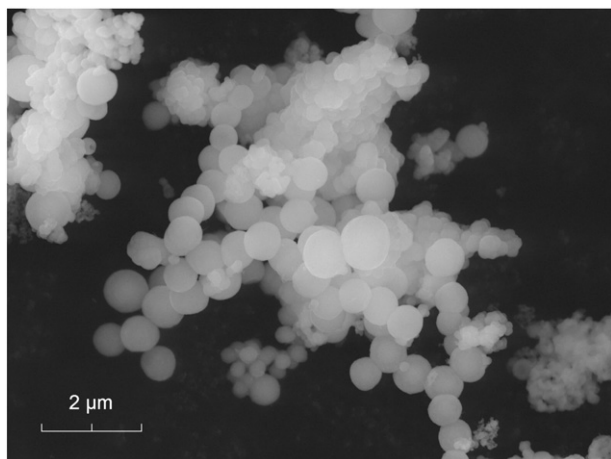


Fig. 3. SEM (SE detector, accelerating voltage 30 kV) image of CdTe prepared at 160 °C.

10² nm, but also bigger particles. Particle size distribution of prepared HgTe is similar to CdTe. Let us emphasize that no capping agent was used in the synthesis.

In addition to cadmium carbonate and mercury oxide, we conducted similar reactions with other metal carbonates and oxides under conditions identical to those described above for reactions with CdCO₃ and HgO. Reactions with lead carbonate, zinc carbonate and antimony oxide produced appropriate tellurides, but the products were not quite pure.

In conclusion, in this article we report a new preparation method of cadmium and mercury telluride via a one pot system using cadmium carbonate (or mercury oxide, respectively), elemental tellurium and bis(diphenylphosphino)amine as the starting materials. The advantage of this method is connected with the elimination of several reaction steps, as the whole process takes place in one step. The formed product is just to be collected, washed and dried. This new synthetic approach seems to be suitable for the metal telluride synthesis, after the appropriate adjustment of the reaction conditions.

Acknowledgements

We would like to acknowledge the assistance of Dr. Katerina Klosova and the TESCAN company in SEM imaging and EDX analysis.

This work was partly supported by the project “CEITEC – Central European Institute of Technology” (CZ.1.05/1.1.00/02.0068).

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