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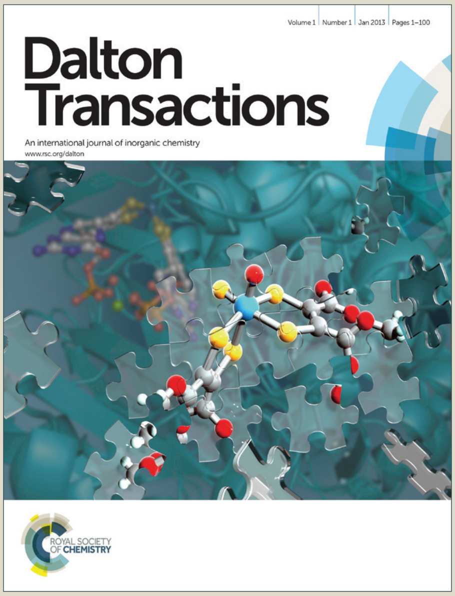

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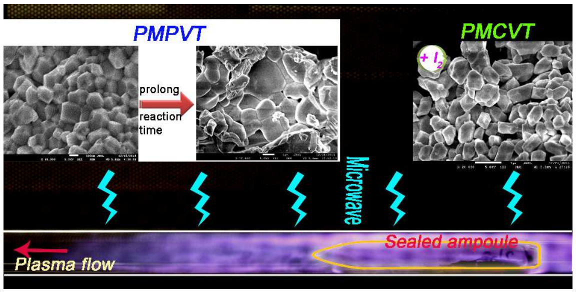
Plasma-enhanced Microwave Solid-state Synthesis of Cadmium Sulfide: Reaction Mechanism and Optical Properties

Ke-zhao Du,[a, b] Apoorva Chaturvedi,[a] Xing-zhi Wang,[b] Yi Zhao,[a] Ke-ke Zhang,[a] Muhammad Iqbal Bakti Utama,[b] Peng Hu,[a] Hui Jiang,[a] Qi-hua Xiong,[b] Christian Kloc[a*]



CdS and other II-VI compounds were synthesized and crystallized in sealed quartz ampoules by a plasma-enhanced microwave vapor transport.

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Plasma-enhanced Microwave Solid-state Synthesis of Cadmium Sulfide: Reaction Mechanism and Optical Properties

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CdS synthesis by plasma-enhanced microwave physical vapor transport (PMPVT) has been developed in this work. The photoluminescence (PL), absorbance, Raman spectra and the mechanism of CdS crystal growth has been investigated. Furthermore, plasma-enhanced microwave chemical vapour transport (PMCVT) synthesis of CdS with additional chemical transport agents has been explored. In addition, other II-VI chalcogenides were also synthesized by PMPVT.

The development of new or improved synthesis methods is one of the ultimate objectives in materials science.[1] II-VI chalcogenide is an important kind of semiconducting material, which have many applications such as laser cooling,[2, 3] light-emitting diode[4, 5] and gamma-detectors.[6, 7] Solid state synthesis of these materials is favourable to solution growth of II-VI chalcogenides, because there are no contamination from solvents and risk of highly toxic gas, such as H_2S and H_2Se.[8] Apart from conventional resistance heating synthesis, microwave heating for rapid synthesis is a useful option. During conventional heating, the energy is transferred by radiant or convective heat flows. Microwave heating primarily results from the interaction between an electromagnetic wave and dielectric materials and is characterized by direct heating, volumetric heating, instantaneous heating and selective heating.[9] The significant advantages of microwave heating include fast on and off switching and rapid energy transfer.[10, 11] Solution-phase microwave chemistry has been well developed; however, comparatively a little work has been carried out in the solid state.[9, 11-14] With respect to the interaction with microwaves, solid materials can be divided into three categories: absorbers, transmitters and reflectors. Microwave absorbers with high dielectric loss tangents couple with microwave energy very well and the microwave reaction could be easily launched. However, the microwave reactions of transmitters and reflectors, such as glasses or metals, are more complex. For conductive materials, the microwave reaction could be driven by fast resistive heating from the eddy currents in the sample induced by the alternating microwave field.[15, 16] Due to dramatic electric discharge, bulk metal is unsuitable for microwave solid-state reactions. Replacing the bulk metal with the corresponding metal powder could avoid this problem. Unfortunately, microwave solid-state reactions involving metal powders are difficult to launch. Several solutions have been found. The first is adding some susceptors (e.g., C, SiC and CuO) as a heat source.[9, 15, 17] The second is providing a large enough amount (above 1.0 gram) of metal powder to support the 'thermal runaway' necessary to drive microwave reactions.[18-21] The third is exposing the reactants to the microwave-induced plasma (MIP) to improve the microwave dielectric heating.[22-28] However, adding the susceptors would contaminate the products and amount requirement of metal powder may be unachievable for different systems or reactions. The MIP method appears to be preferable, except that the volatile reactants or products exposed under the plasma heating, which could reach temperatures in excess of 1000 ℃ *via* ion bombardment, may evaporate from the reactor.[26] Moreover, the mechanisms have rarely been discussed. Therefore, the solid-state microwave reactions involving metal powders still need improvement.

So far, reports on the microwave solid-state synthesis of chalcogenide materials by direct combination of the appropriate elemental powders are limited.[19-21, 23, 25, 29-32] Most of the II-VI semiconductors synthesized by microwave have involved solution-based process.[33-46] To the best of our knowledge, there are no reports of CdX (X =S, Se, Te) prepared *via* microwave solid-state synthesis.

Herein, we developed plasma-enhanced physical vapor transport (PMPVT) of II-VI chalcogenides including CdX. All of the starting materials were sealed in quartz ampoules to prevent the loss of the reactants or products under plasma flow. There were no additional susceptors as a heat source or lower limit on the amount of metal powders required to activate the reactions. Taking CdS as an example, the crystal growth and mechanism were studied by Energy Dispersive X-Ray Spectroscopy (EDX), powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). The photoluminescence (PL), absorbance and Raman spectra of CdS have also been studied. Furthermore, plasma-enhanced microwave chemical vapour transport (PMCVT) of CdS with an additional chemical transport agent was also developed.

The detail of the experiments could be found in the Supporting Information. In a typical experiment, fine powders of respective metals and chalcogens (100~200 mg of mixture) were sealed in a quartz ampoule with approximately 10 torr pressure of argon. Then, the ampoules were placed in a quartz tube that was located in the center of a modified domestic microwave oven (2450 MHz, 1 kW) without any additional conventional heating (Fig. 1). The argon gas flowed through the evacuated quartz tube under 5 ~ 10 torr pressure. When the microwave oven was running, the argon plasma in the quartz tube was ignited and could be seen visually inside the quartz tube. At the end of the experiment the ampoule was cooled and a small amount of chalcogen was usually condensed in the top of ampoule. Therefore, the excess chalcogen is necessary for a complete reaction, especially for sulfide (Fig. S1). All the characterizations, including SEM, EDS, Raman, PL and absorbance, were performed on the samples confirmed by PXRD first.

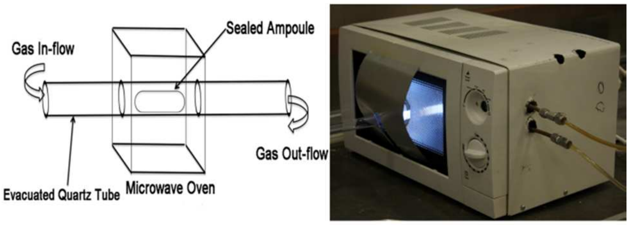


Fig. 1 Schematic diagram of the plasma-enhanced microwave set enclosed inside a Faraday cage for safety reason.

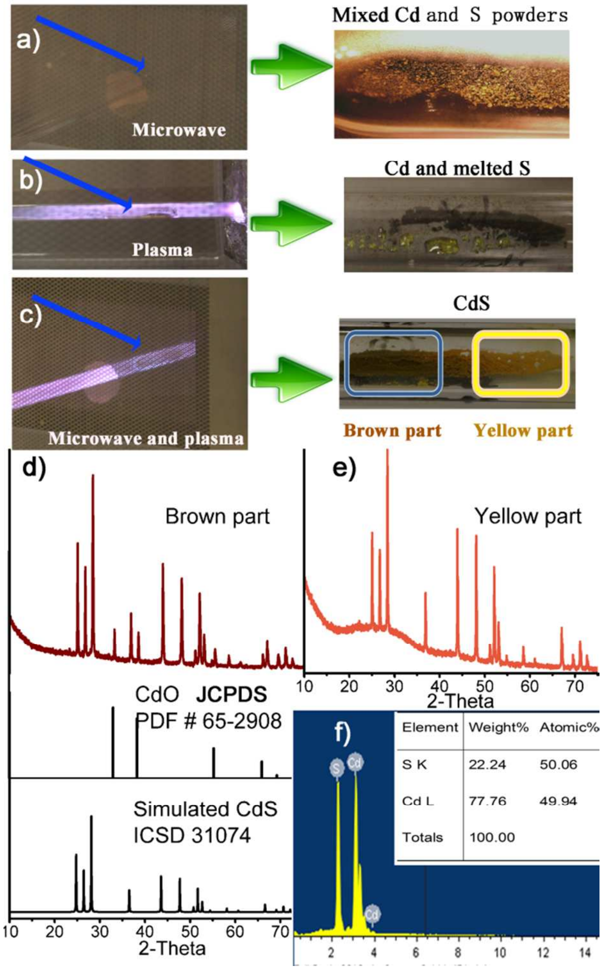
To determine the major driving force of PMPVT, three control experiments were performed (Fig. 2a, b, c) as follows. In all three experiments, 10 torr Ar was inside the sealed ampoule.

a) Microwave heating without plasma: The sealed ampoule with reactants underwent 2 hours of microwave irradiation. Plasma in quartz tube was not formed due to the atmospheric Ar pressure. Unreacted Cd and S powders were obtained (Fig. 2a).

b) Plasma heating outside the microwave oven: Plasma was ignited inside the quartz tube. The sealed ampoule underwent 2 hours of plasma soaking outside the microwave oven. Unreacted Cd powder and melted S were obtained (Fig. 2b).

c) Plasma-enhanced microwave heating: Plasma was ignited inside the quartz tube. The sealed ampoule inside the microwave oven underwent 2 hours of microwave irradiation with plasma surrounding it. A well synthesized CdS product was obtained (Fig. 2c).

The PXRD patterns of the products confirmed that there was no CdS phase under the unimodal microwave or plasma heating (Fig. S2). The microwave irradiation could not melt the S due to the poor microwave coupling of the Cd and S powders (experiment a). Although the plasma melted the S within one minute, it still could not drive the reaction between Cd and S (experiment b). Only when the sealed ampoule was placed in the microwave oven with plasma surrounding, a CdS product with two different colors was synthesized (experiment c). According to the PXRD results (Fig. 2d. e), the yellow part was pure CdS, whereas the brown part contained CdO impurities. From the PXRD results of commercial Cd powder (Fig. S3), it was clear that the CdO impurity came from the commercial Cd powder starting material. The Cd:S ratio of the yellow part is 49.94:50.06 closed to 1:1 as the Fig. 2f shown.



Element	Weight%	Atomic%
S K	22.24	50.06
Cd L	77.76	49.94
Totals	100.00	

Fig. 2 The phenomena of the three control experiments (a, b, c), PXRD patterns of the brown part (d) and the yellow part (e) and EDX (f) of the CdS product. The blue arrows point to the positions of the amouples.

Plasma is an ionized gas with an equal density of positive and negative charges. The collision between the ionized gas and the ampoule can heat the reactants. In a microwave cavity, the increased temperature improves the microwave dielectric heating of the reactants and promote the microwave reactions. This phenomenon is similar to MIP experiments.[22-28] And the vacuum inside the ampoule could also affect the progress of the reaction. When the ampoule was evacuated to a vacuum of 1.5×10^{-4} torr, the PXRD shown much smaller peak intensity of CdS compared with CdO and unreacted S could be found in the mixture (Fig 3). This result suggested that the reaction in high vacuum was not as complete as the one in 10 torr, which may be due to the secondary plasma inside the ampoule. As previously reported, the primary plasma could induce optical emission called vacuum-ultraviolet (VUV) radiation.[47, 48] The VUV radiation could be transmitted into the ampoule and reacted with the ground state molecules in the gas inside the ampoule.[47] Then, the secondary plasma would be generated and further promotes the microwave reaction. Therefore, the plasma surrounding the ampoule played an additional role besides heating in PMPVT.

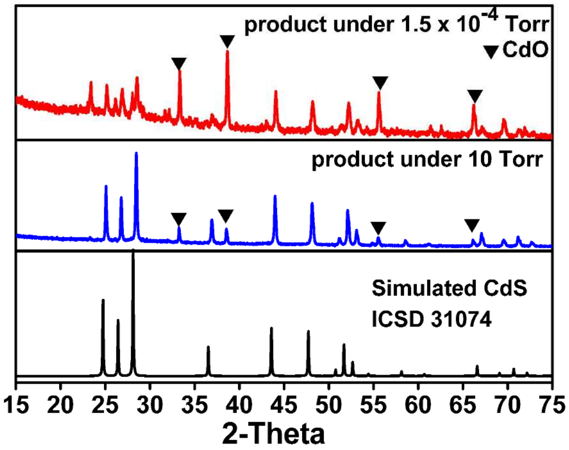


Fig. 3 PXRD patterns of the products synthesized by PMPVT under different pressures inside the ampoules.

Time-dependent experiments were carried out to understand the crystal growth (Fig. S4). As shown in the SEM images in Fig. 4, the regular crystal plane could be easily found within 30 minutes of reaction. If the reaction time was prolonged, the crystal grain became larger (Fig. S5) and more irregular. The mechanism of CdS crystal growth in the plasma enhanced microwave field is described below.

At the beginning of the reaction, the plasma heated the reactants. The increased temperature improved the microwave dielectric heating of the materials. In addition to the secondary plasma inside the ampoule, the inter-diffusion between Cd and S was enhanced by microwave irradiation.[26] CdS crystallites were quickly formed. Then, the microwave dielectric heating of CdS caused the coalescence of individual crystallites. The enhanced interface ion diffusion dominated the reaction and disturbed the ordered growth of the crystal.[49, 50] Finally, what we found most was a round crystal grain in the product.

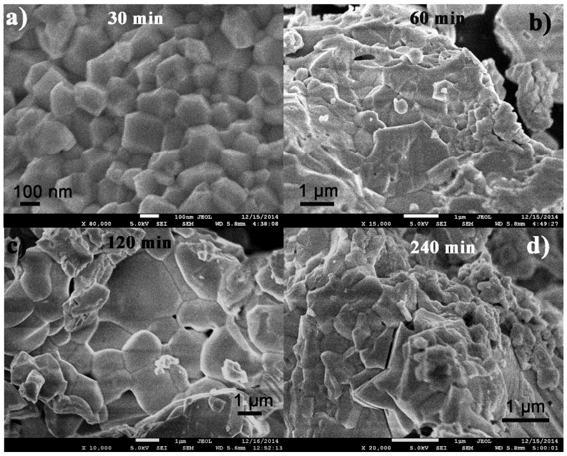


Fig. 4 SEM images of CdS with different reaction times synthesized by PMPVT. 30 min (a), 60 min (b), 120 min (c) and 240 min (d).

The PL, absorbance and Raman spectra of CdS, which was synthesized by PMPVT, were also studied (Fig. 5). A strong PL peak at approximately 517.5 nm (2.40 eV) was found, which could be assigned to interstitial sulfur.[51, 52] A smaller shoulder peak at approximately 533.6 nm (2.32 eV) could also be fitted. This peak should be due to the recombination of donor-acceptor pairs (DAP, 2.34 eV), in which sulfur vacancy and cadmium vacancy were suggested as the donor and acceptor, respectively.[53-55] The Urbach tail is an exponential band-tail of state, which can be caused by the interaction between electron and impurity, hole or phonon,[56, 57] The absorbance curve allows us to observe the Urbach tail directly from Fig. 5a.

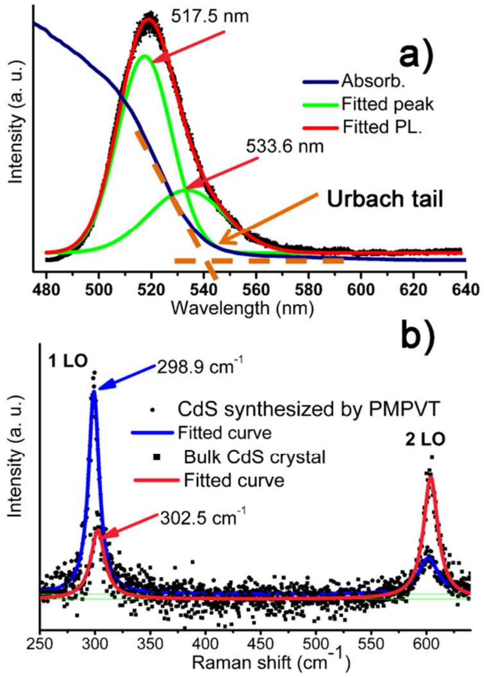


Fig. 5 PL (a, black dot), absorbance (a, blue line) and Raman (b) spectra of CdS. The red and green lines in the PL spectra are the curves fitted by a Gaussian function. The Raman spectra are the curves fitted by a Lorentzian function. The yellow dashed lines indicate the Urbach tail. The excitation wavelengths of PL and Raman are 473 nm and 532 nm, respectively.

In Fig. 5b, two strong Raman peaks of CdS at approximately 300 and 600 cm^{-1} were attributed to first order (1 LO) and second order (2 LO) scattering of longitudinal optical phonon A1 modes, respectively. There was a remarkable blue shift (~3.6 cm^{-1}) of the 1 LO peak in the product of PMPVT compared with the bulk CdS crystal. This result should be due to the lattice contraction induced by the large surface tension of the nanocrystal grain.[51, 58, 59]

Other chalcogenides in the II-VI group could also be synthesized in the same way. The EDX, SEM images and related PXRD patterns are shown in table S1. Most of the crystal grains were as irregular as CdS. In telluride, there was small amount of metal tellurium trioxide due to the TeO_2 impurity in Te powders (Fig. S3).

In conventional solid-state synthesis, chemical vapor transport (CVT) is usually used. Iodine is a common transport agent in the solid-state synthesis of II-VI crystals, which could improve the formation of crystalline solids.[60] Therefore the applicability of iodine in PMPVT was explored, and some iodine was added as a transport chemical in the synthesis of CdS. Bright yellow light could be seen in the sealed ampoule during the reaction (Fig. 6a). When the reaction was finished, almost the entire product was a yellow powder, and PXRD result confirmed the pure phase of CdS (Fig. 6b) without CdO impurity. The mechanism of PMCVT should be related to equations (1), (2) and (3).[60, 61] In addition, we believe that the intermediate CdI_2 would increase the microwave absorption and accelerate the reaction.[15] In this case, the CdS product was composed of dispersive particles (Fig. 6c and 6d). These results suggested that the transport agent could improve the physical vapor transport of II-VI compounds.

$$\mathbf{Cd} + \mathbf{I_2} \rightleftharpoons \mathbf{CdI_2} \quad (1)$$

$$\mathbf{2CdO} + \mathbf{2I_2} \rightleftharpoons \mathbf{2CdI_2} + \mathbf{O_2} \quad (2)$$

$$\mathbf{CdI_2} + \mathbf{S} \rightleftharpoons \mathbf{CdS} + \mathbf{I_2} \quad (3)$$

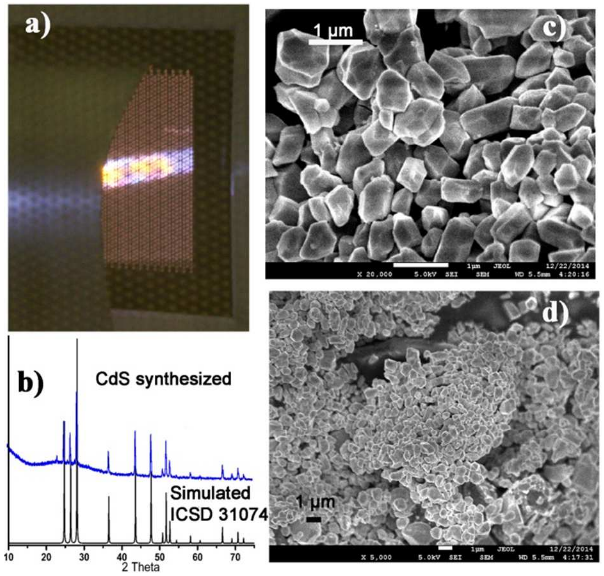


Fig. 6 Phenomenon of PMCVT reaction(a); PXRD patterns (b) and SEM images (c, d) of the product.

In conclusion, II-VI group chalcogenides were successfully synthesized by PMPVT. In this method, there are no additional susceptors or lower limit on the amount of metal powders required to activate the reactions. All of the reactants were carried in sealed quartz ampoules to prevent losses of reactants or products under plasma flow. The mechanism of CdS crystal growth involved plasma-enhanced microwave activity, secondary plasma, inter-diffusion and interface diffusion. The PL spectrum showed that interstitial sulfur in the CdS synthesized by PMPVT was a dominated defect. Adding the transport agent further improved the plasma-enhanced microwave synthesis of CdS (PMCVT). The plasma-enhanced microwave solid-state synthesis could be applicable to numerous other inorganic binary and multinary compounds.

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Notes and references

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†Electronic Supplementary Information (ESI) available: The detail of the chemicals, PMPVT and PMCVT experiments; the PXRD of starting materials and products under different conditions; the SEM, EDX and PXRD of other II-VI chalcogenides. See DOI: 10.1039/c000000x/

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