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A new low temperature one-step route to metal chalcogenide semiconductors: PbE, Bi_2E_3 ($E = S$, Se, Te)

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A solvothermal reaction of metal oxalates such as PbC_2O_4, $Bi_2(C_2O_4)_3$ with E ($E = S$, Se, Te) in organic solvents at relatively low temperature (120–160 °C) produces crystalline PbS, PbSe, PbTe, Bi_2S_3, Bi_2Se_3, and Bi_2Te_3:

$$PbC_2O_4 + E \xrightarrow{\text{solvent}} PbE + 2CO_2\uparrow$$

$$Bi_2(C_2O_4)_3 + 3E \xrightarrow{\text{solvent}} Bi_2E_3 + 6CO_2\uparrow$$

Recently, the synthesis of binary metal sulfides, selenides and tellurides of groups 12, 14 and 15 has been the focus of attention because of their important physical and chemical properties,[1–13] good commercial applications in semiconductors, pigments, luminescence devices,[14] solar cells, IR detectors, and optical fiber communications,[15] and modern thermoelectric coolers.[6,10,11] Especially, with the planned phase-out of chlorofluorocarbon (CFC) refrigerants within this decade, the synthesis of Bi_2Te_3, which is the most efficient semiconductor material for modern thermoelectric cooling devices, has been the focus of recent research.[5–13]

Conventionally, metal chalcogenides are synthesized by the reaction of the elements at elevated temperature, typically 500–600 °C, in evacuated tubes,[1,16–18] by a solid state metathesis reaction of anhydrous metal halide with Na_2(S,Se) or Li_2(S,Se,Te)[19] at high temperature, typically 500 °C, or involved the use of complex and expensive organometallic precursors,[3,8,9,11–13,20,21] or by reaction of aqueous metal salt solutions with the highly toxic and malodorous gaseous H_2S, H_2Se, H_2Te.[22,23] Moreover, H_2Te is unstable at room temperature, decomposing into hydrogen and metallic tellurium, which results in impurities in the final product.[7]

Recently, Parkin *et al.*[1,2] reported a new method for synthesizing metal chalcogenides by a reaction between metal and E in liquid ammonia at room temperature. Crystalline PbS and PbSe powders were obtained at room temperature.[1] However, the reaction of lead with tellurium in liquid ammonia did not form PbTe.[2] Ritter *et al.*[10] reported a new two-step process for the preparation of polycrystalline Bi_2Te_3 by reduction of a complex precursor ($Bi_2O_3 \cdot 3TeO_2 \cdot xH_2O$) with hydrogen at 275 °C. Our group successfully prepared Bi_2S_3 nanorods by a solvothermal reaction between bismuth trichloride and thiourea in ethanol at 140 °C.[24] In addition, nanocrystalline β-In_2S_3 was also prepared in organic madia in our laboratory.[25]

Here we report a novel low temperature one-step route to crystalline PbE and Bi_2E_3 by a solvothermal reaction between metal oxalates and E in organic solvents such as ethylenediamine (en) and pyridine (py). The reactions can be expressed by eqn. (1) and (2):

$$PbC_2O_4 + E \xrightarrow{\text{solvent}} PbE + 2CO_2\uparrow \quad (1)$$

$$Bi_2(C_2O_4)_3 + 3E \xrightarrow{\text{solvent}} Bi_2E_3 + 6CO_2\uparrow \quad (2)$$

In a typical procedure, 0.01 mol analytical S (or Se, Te) and 0.01 mol analytical PbC_2O_4 were put into a Teflon-lined autoclave of 100 ml capacity, which was filled with py or en to 80% of the total volume. The autoclave was sealed and maintained at 140 °C for 6–12 h and then allowed to cool to room temperature. The dark grey precipitate was filtered and washed with ethanol, distilled water, dilute HNO_3 solution, and absolute ethanol several times to remove the impurities. The product was dried in vacuum at 70 °C for 4 h.

Reaction of PbC_2O_4 with E ($E = S$, Se, Te) produced crystalline PbS, PbSe, and PbTe. All the products were characterized by X-ray powder diffraction.‡ XRD patterns show that the as-prepared PbS, PbSe and PbTe powders were pure cubic phases. The X-ray powder diffraction data for the synthesized metal chalcogenides are summarized in Table 1. The cell parameters are in good agreement with the reported data. The TEM image§ in Fig. 1(a) shows that the PbSe powders synthesized in en consist of uniform square particles with an average size of 80 nm, which is in good agreement with the average size calculated by the Scherrer equation. TEM observation indicates that the PbTe powders produced consist of agglomerates of particles with irregular shape. Elemental analysis¶ show that the compositions of the products are PbS, PbSe, and PbTe, which are consistent with the calculated results by XPS.

The reaction of bismuth oxalate with sulfur, selenium and tellurium proceeded similarly to that of lead oxalate. The produced Bi_2S_3, Bi_2Se_3, and Bi_2Te_3 powders display the expected colours of the metal chalcogenides. The Bi_2S_3, Bi_2Se_3 powders produced are the pure orthorhombic phase and hexagonal phase, respectively, the cell parameters of which are also in excellent agreement with the reported data as shown in Table 1. The TEM image in Fig. 1(b) indicates that the Bi_2Se_3 powders display flake-like morphology. The selected

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‡X-Ray diffraction analysis was performed using a Japan Rigaku D/Max-γA X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å), employing a scanning rate of 0.02 ° s^{-1} in the 2θ range from 10° to 60°.

§TEM images and selected area electron diffraction (ED) patterns were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

¶Elemental analysis by atomic absorption on a Perkin-Elmer 1100B atomic absorption spectrophotometer. X-Ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg-Kα X-rays as the excitation source.

Table 1 X-Ray crystallographic data for metal chalcogenides synthesized by the present route

reagents	crystalline phase detected[26]	lattice parameters/nm	reference lattice parameters/nm[26]
PbC_2O_4+S	PbS	$a=0.59340$	$a=0.59362$
PbC_2O_4+Se	PbSe	$a=0.6126$	$a=0.6124$
PbC_2O_4+Te	PbTe	$a=0.6447$	$a=0.6443$
$Bi_2(C_2O_4)_3+S$	Bi_2S_3	$a=1.1150$, $b=1.1306$, $c=0.3980$	$a=1.1149$, $b=1.1304$, $c=0.3981$
$Bi_2(C_2O_4)_3+Se$	Bi_2Se_3	$a=0.4141$, $c=2.875$	$a=0.4133$, $c=2.862$
$Bi_2(C_2O_4)_3+Te$	Bi_2Te_3+Te	$a=0.43852$, $c=3.0484$	$a=0.43772$, $c=3.0483$

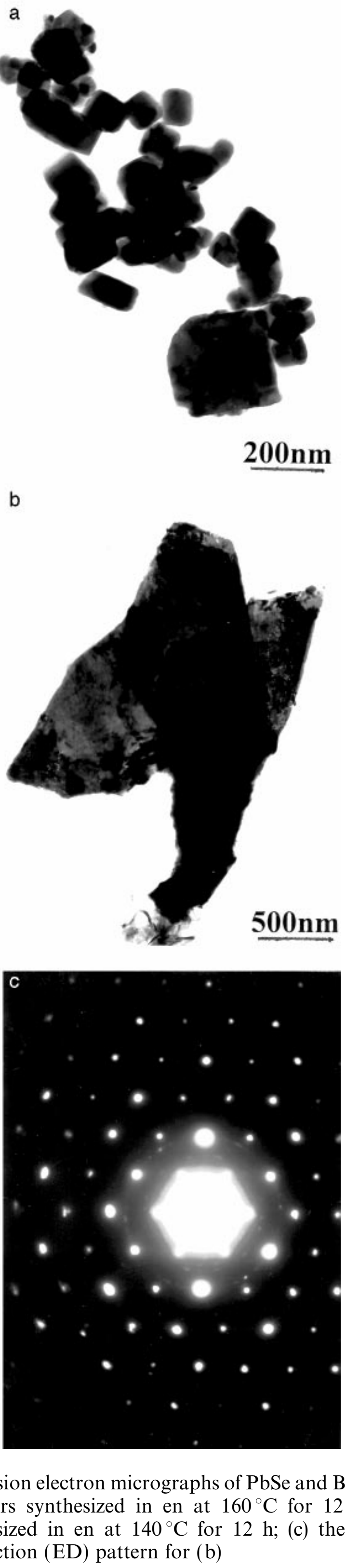

Fig. 1 Transmission electron micrographs of PbSe and Bi_2Se_3 powders: (a) PbSe powders synthesized in en at 160 °C for 12 h; (b) Bi_2Se_3 powders synthesized in en at 140 °C for 12 h; (c) the selected area electronic diffraction (ED) pattern for (b)

area electronic diffraction (ED) pattern [Fig. 1(c)] for the sample in Fig. 1(b) demonstrates that the Bi_2Se_3 powders are single crystalline. Elemental analysis¶ and the XPS analysis show that the compositions of the products are Bi_2S_3, Bi_2Se_3. The produced Bi_2Te_3 sample can be indexed as a hexagonal phase. However, a small amount of Te was detected by XRD in the Bi_2Te_3 synthesized by the present process.

The effects of solvents on the synthesis of crystalline PbE and Bi_2E_3 were investigated. We found that crystalline powders of PbE can be prepared both in py and in en at 120–160 °C; however, X-ray diffraction spectra indicated the presence of some Se, Te in the samples PbSe and PbTe synthesized in py. Similar phenomena are observed in the synthesis of crystalline Bi_2Se_3 and Bi_2Te_3. These results indicated that solvents en and py have different influences on the completeness of the solvent thermal reaction, and the reaction in en is more complete.

The influences of temperature and time on the synthesis of crystalline PbE and Bi_2E_3 were also studied. If the temperature is lower than 120 °C, the reaction is very incomplete and sometimes can not be initiated. The reaction is also incomplete if the time is shorter than 6 h. It was found that some metallic Bi will be present in the final product Bi_2E_3 when the temperature exceeds 160 °C, even though $Bi_2(C_2O_4)_3$ is not in excess. We believe that this results from the decomposition of $Bi_2(C_2O_4)_3$ in the system at higher temperature. However, no metallic Pb was detected by XRD even at temperatures up to 180 °C or in the presence of an excess of PbC_2O_4. These results revealed that the optimum conditions for the synthesis of PbE and Bi_2E_3 are at 120–160 °C for 6–12 h.

In conclusion, a new low temperature one-step route to metal chalcogenides was successfully developed. This simple route effectively avoids the use of expensive organometallic precursors and malodorous H_2S, H_2Se, H_2Te, and prevents the release of toxic gases. We are beginning to extend this synthetic route to the preparation of other important metal chalcogenides.

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