APPENDICES

APPENDIX A

The Joint Committee for Powder Diffraction Standards (JCPDS) [80]

1. CuS, JCPDS file number 06-0464

Name and formula

Reference code:	06-0464
Mineral name:	Covellite, syn
PDF index name:	Copper Sulfide
Empirical formula:	CuS
Chemical formula:	CuS

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P63/mmc
Space group number:	194
a (Å):	3.7920
b (Å):	3.7920
c (Å):	16.3440
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	120.0000
Calculated density:	4.68

Measured density:	4.67
Volume of cell:	203.53
Z:	6.00
RIR:	-

Subfiles and Quality

Subfiles:	Inorganic
	Mineral
	Alloy, metal or intermetalic
	Corrosion
	Common Phase
	Educational pattern
	Forensic
	NBS pattern
	Superconducting Material
Quality:	Star (S)

Comments

Color:	Dark blue
General comments:	Opaque mineral optical data on specimen from unspecified locality: R_1R_o=7.1, RR_2R_e=23.7, Disp.=16, VHN_{100}=128-138, Color Values=o .224, .226, 6.8, e .283, .287, 23.5, Ref.: IMA Commission Ore Microscopy QDF. Measured density and color from *Dana's System of Mineralogy, 7th Ed.*, **I**.
Sample source:	Sample from Fisher Scientific Company.
Sample preparation:	Annealed at 400 ^oC for several hours in sulfur atmosphere.

Analysis:	Spectroscopic analysis: <0.1% Si, Zn; <0.01% Ag, Al, Ca, Fe, Mg, Ni; <0.001% B, Mn, Pb.
Optical data:	B=1.45, Sign=+
Additional pattern:	To replace 1-1281, 3-724 and 3-1090 and validated by calculated pattern 24-60. See ICSD 24586 and 36155 (PDF 76-1725); See ICSD 63327 (PDF 78-2121).
Temperature:	Pattern taken at 26 ^{o}C.

References

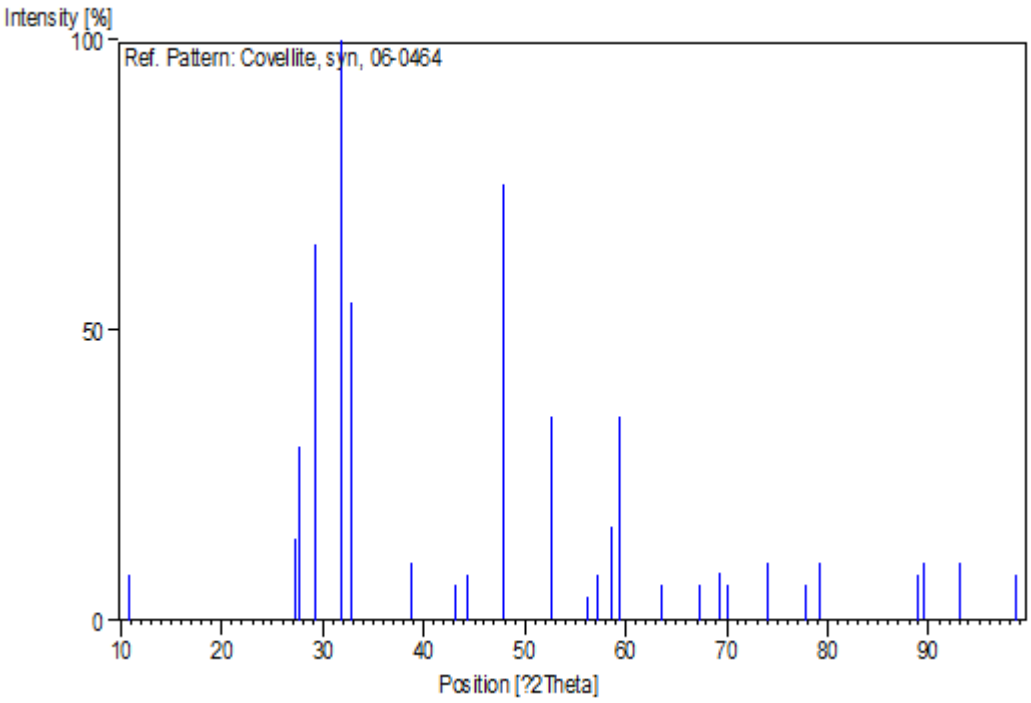
Primary reference: *Natl. Bur. Stand. (U.S.), Circ. 539*, **IV**, 13, (1955)

Peak list

No.	h	k	l	d [A]	I [%]
1	0	0	2	8.18000	8.0
2	1	0	0	3.28500	14.0
3	1	0	1	3.22000	30.0
4	1	0	2	3.04800	65.0
5	1	0	3	2.81300	100.0
6	0	0	6	2.72400	55.0
7	1	0	5	2.31700	10.0
8	1	0	6	2.09700	6.0
9	0	0	8	2.04300	8.0
10	1	0	7	1.90200	25.0
11	1	1	0	1.89600	75.0
12	1	0	8	1.73500	35.0
13	2	0	1	1.63400	4.0
14	2	0	2	1.60900	8.0
15	2	0	3	1.57200	16.0
16	1	1	6	1.55600	35.0

17	1	0	10	1.46300	6.0
18	1	1	8	1.39000	6.0
19	1	0	11	1.35400	8.0
20	2	0	7	1.34300	6.0
21	2	0	8	1.28000	10.0
22	2	1	2	1.22700	6.0
23	2	1	3	1.21000	10.0
24	1	0	14	1.09980	8.0
25	3	0	0	1.09460	10.0
26	2	1	8	1.06070	10.0
27	3	0	6	1.01550	8.0

Stick Pattern



2. Al, JCPDS file number 01-1176

Name and formula

Reference code:	01-1176
PDF index name:	Aluminum
Empirical formula:	Al
Chemical formula:	Al

Crystallographic parameters

Crystal system:	Cubic
Space group:	Fm3m
Space group number:	225
a (Å):	4.0406
b (Å):	4.0406
c (Å):	4.0406
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	90.0000
Measured density:	2.69
Volume of cell:	65.97
Z:	4.00
RIR:	-

Status, subfiles and quality

Status:	Marked as deleted by ICDD
Subfiles:	Inorganic
Quality:	Blank (B)

Comments

Deleted by:	Deleted by NBS card.
Color:	White
Melting point:	660 ^{o}C

References

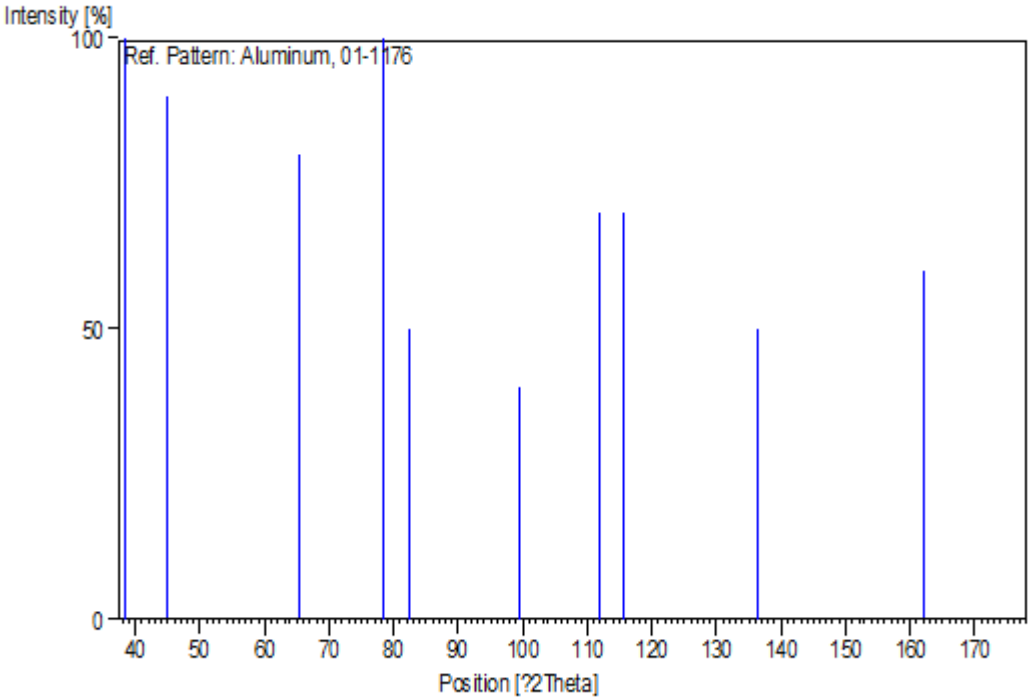
Primary reference:	Davey., *Phys. Rev.*, **25**, 753, (1925)
Optical data:	*Data on Chem. for Cer. Use, Natl. Res. Council Bull. 107*
Unit cell:	*The Structure of Crystals, 1st Ed.*

Peak list

No.	h	k	l	d [A]	I [%]
1	1	1	1	2.34000	100.0
2	2	0	0	2.02000	90.0
3	2	2	0	1.43000	80.0
4	3	1	1	1.22000	100.0
5	2	2	2	1.17000	50.0
6	4	0	0	1.01000	40.0
7	3	3	1	0.93000	70.0
8	4	2	0	0.91000	70.0
9	4	2	2	0.83000	50.0

10	5	1	1	0.78000	60.0
11				0.72000	20.0

Stick Pattern



3. Sb, JCPDS file number 02-0587

Name and formula

Reference code: 02-0587

PDF index name: Antimony

Empirical formula: Sb

Chemical formula: Sb

Crystallographic parameters

Crystal system: Rhombohedral

Space group:	R-3m
Space group number:	166
a (Å):	4.1110
b (Å):	4.1110
c (Å):	10.7620
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	120.0000
Measured density:	6.67
Volume of cell:	157.51
Z:	2.00
RIR:	-

Status, subfiles and quality

Status:	Marked as deleted by ICDD
Subfiles:	Inorganic
Quality:	Doubtful (O)

Comments

Deleted by:	Deleted by NBS.
Color:	Tin white
General comments:	Photographed at 2122 C.
Melting point:	630.5
Unit cell:	Rhombohedral cell: a=4.301, a=57.08.

References

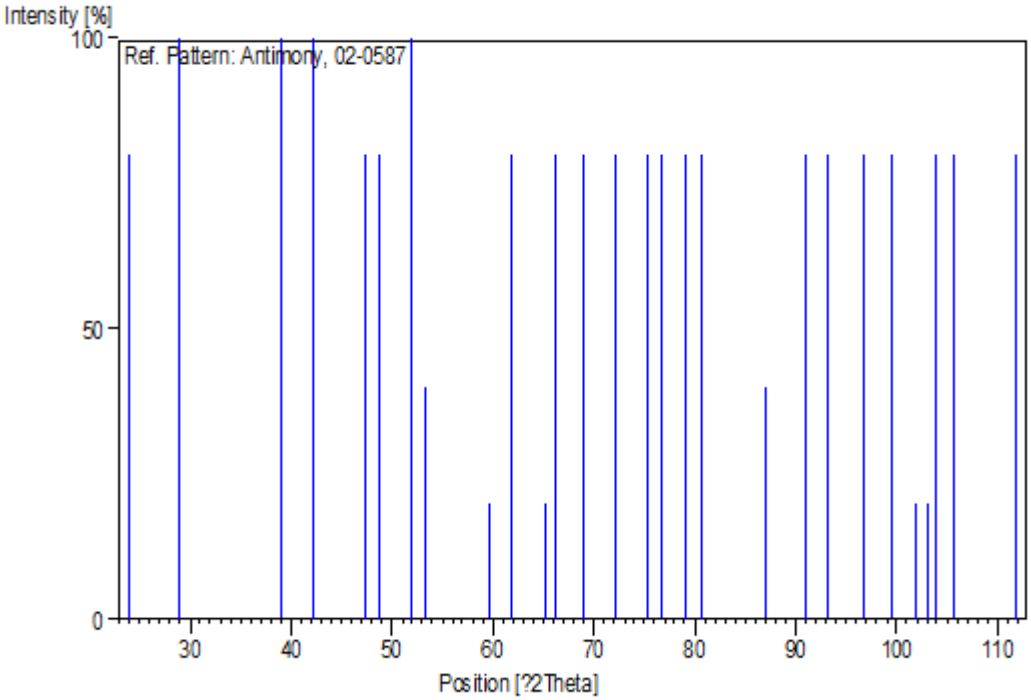
Primary reference: Dorn, Glockler., *J. Phys. Chem.*, **41**, 502, (1937)

Peak list

No.	h	k	l	d [A]	I [%]
1				3.71000	80.0
2				3.08000	100.0
3				2.31000	100.0
4	1	0	4	2.14000	100.0
5				1.92000	80.0
6				1.87000	80.0
7	0	2	1	1.76000	100.0
8				1.72000	40.0
9				1.55000	20.0
10				1.50000	80.0
11				1.43000	20.0
12	1	0	7	1.41000	80.0
13	1	1	6	1.36000	80.0
14	1	2	2	1.31000	80.0
15	0	1	8	1.26000	80.0
16				1.24000	80.0
17				1.21000	80.0
18	3	0	0	1.19000	80.0
19				1.12000	40.0
20				1.08000	80.0
21				1.06000	80.0
22	1	0	10	1.03000	80.0
23	2	1	7	1.01000	80.0
24	3	0	6	0.99200	20.0
25	1	3	1	0.98400	20.0
26				0.97800	80.0
27				0.96700	80.0

28	0.93000	80.0

Stick Pattern



4. Sb, JCPDS file number 02-0592

Name and formula

Reference code: 02-0592

PDF index name: Antimony

Empirical formula: Sb

Chemical formula: Sb

Crystallographic parameters

Crystal system: Rhombohedral

Space group:	R-3m
Space group number:	166
a (Å):	4.3000
b (Å):	4.3000
c (Å):	11.2500
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	120.0000
Measured density:	6.67
Volume of cell:	180.14
Z:	2.00
RIR:	-

Status, subfiles and quality

Status:	Marked as deleted by ICDD
Subfiles:	Inorganic
Quality:	Blank (B)

Comments

Deleted by:	Deleted by NBS.
Color:	Tin white
Sample source:	Specimen from White River, California, USA.
Melting point:	630.5
Unit cell:	Rhombohedral cell: a=4.4976, a=57.11.

References

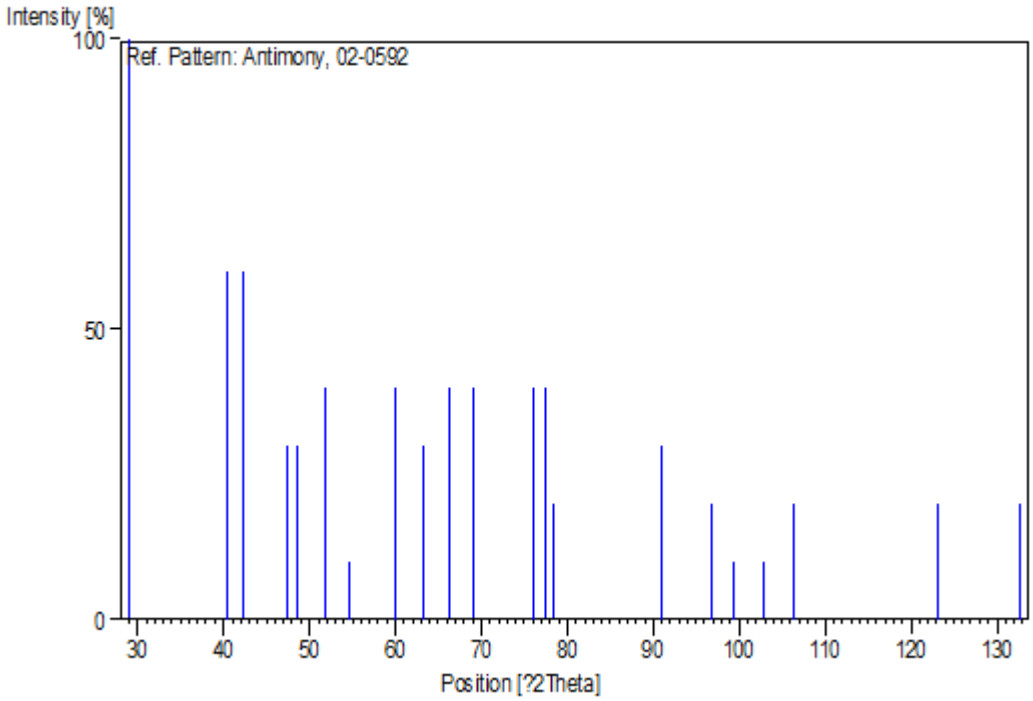
Primary reference: Harcourt, G., *Am. Mineral.*, **27**, 63, (1942)

Unit cell: *The Structure of Crystals, 1st Ed.*

Peak list

No.	h	k	l	d [A]	I [%]
1	0	1	2	3.07000	100.0
2	1	0	4	2.23000	60.0
3	1	1	0	2.13000	60.0
4	0	1	5	1.92000	30.0
5	1	1	3	1.87000	30.0
6	2	0	2	1.76000	40.0
7				1.68000	10.0
8	0	2	4	1.54000	40.0
9	1	0	7	1.47000	30.0
10	1	1	6	1.41000	40.0
11	1	2	2	1.36000	40.0
12	0	0	9	1.25000	40.0
13	3	0	0	1.23000	40.0
14	0	2	7	1.22000	20.0
15	1	1	9	1.08000	30.0
16	1	3	1	1.03000	20.0
17	3	1	2	1.01000	10.0
18	0	1	11	0.98500	10.0
19	0	2	10	0.96200	20.0
20	2	1	10	0.87600	20.0
21	1	0	13	0.84100	20.0

Stick Pattern



5. Zn, JCPDS file number 04-0831

Name and formula

Reference code:	04-0831
Mineral name:	Zinc, syn
PDF index name:	Zinc
Empirical formula:	Zn
Chemical formula:	Zn

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P63/mmc
Space group number:	194
a (Å):	2.6650
b (Å):	2.6650
c (Å):	4.9470
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	120.0000
Calculated density:	7.13
Measured density:	7.05
Volume of cell:	30.43
Z:	2.00
RIR:	3.80

Subfiles and Quality

Subfiles:	Inorganic
	Mineral
	Alloy, metal or intermetalic
	Common Phase
	Educational pattern
	Explosive
	Forensic
	NBS pattern
	Pigment/Dye
Quality:	Star (S)

Comments

Color:	Bluish white
Sample source:	Sample from New Jersey Zinc Company, Sterling Hill, New Jersey, USA.
Analysis:	Spectroscopic analysis shows faint traces of Pb, Cu, Mg, Si.
Optical data:	B=2.58
Melting point:	420 ^{o}C
Temperature:	Pattern taken at 26 ^{o}C.

References

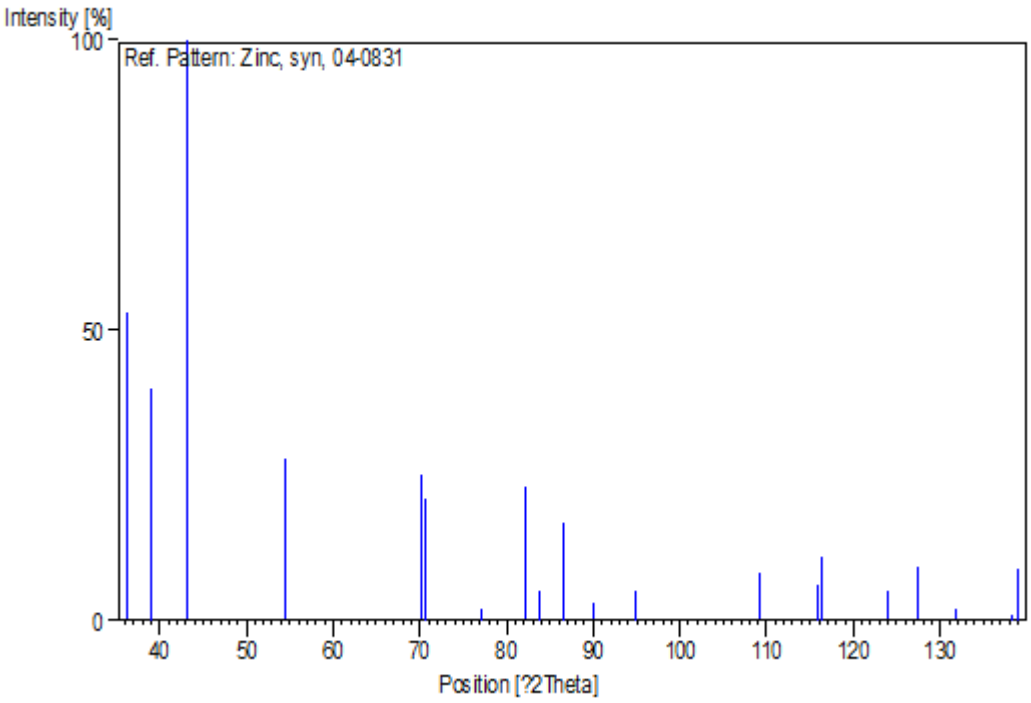
Primary reference:	Swanson, Tatge., *Natl. Bur. Stand. (U.S.), Circ. 539*, **I**, 16, (1953)
Optical data:	Winchell., *Elements of Optical Mineralogy*, 1, (1927)

Peak list

No.	h	k	l	d [A]	I [%]
1	0	0	2	2.47300	53.0
2	1	0	0	2.30800	40.0
3	1	0	1	2.09100	100.0
4	1	0	2	1.68700	28.0
5	1	0	3	1.34200	25.0
6	1	1	0	1.33200	21.0
7	0	0	4	1.23700	2.0
8	1	1	2	1.17290	23.0
9	2	0	0	1.15380	5.0
10	2	0	1	1.12360	17.0
11	1	0	4	1.09010	3.0
12	2	0	2	1.04560	5.0
13	2	0	3	0.94540	8.0
14	1	0	5	0.90930	6.0

15	1	1	4	0.90640	11.0
16	2	1	0	0.87220	5.0
17	2	1	1	0.85890	9.0
18	2	0	4	0.84370	2.0
19	0	0	6	0.82450	1.0
20	2	1	2	0.82250	9.0

Stick Pattern



6. AlSb, JCPDS file number 72-2247

Name and formula

Reference code: **73-2247**

ICSD name: Aluminum Antimony

Empirical formula:	AlSb
Chemical formula:	AlSb

Crystallographic parameters

Crystal system:	**Cubic**
Space group:	F-43m
Space group number:	216
a (Å):	6.1260
b (Å):	6.1260
c (Å):	6.1260
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	90.0000
Calculated density:	4.30
Measured density:	4.34
Volume of cell:	229.90
Z:	4.00
RIR:	14.18

Subfiles and Quality

Subfiles:	**Inorganic**
	Alloy, metal or intermetalic
	Corrosion
	Modelled additional pattern
Quality:	Calculated (C)

Comments

ICSD collection code: **024804**

Test from ICSD: No R value given.

At least one TF missing.

References

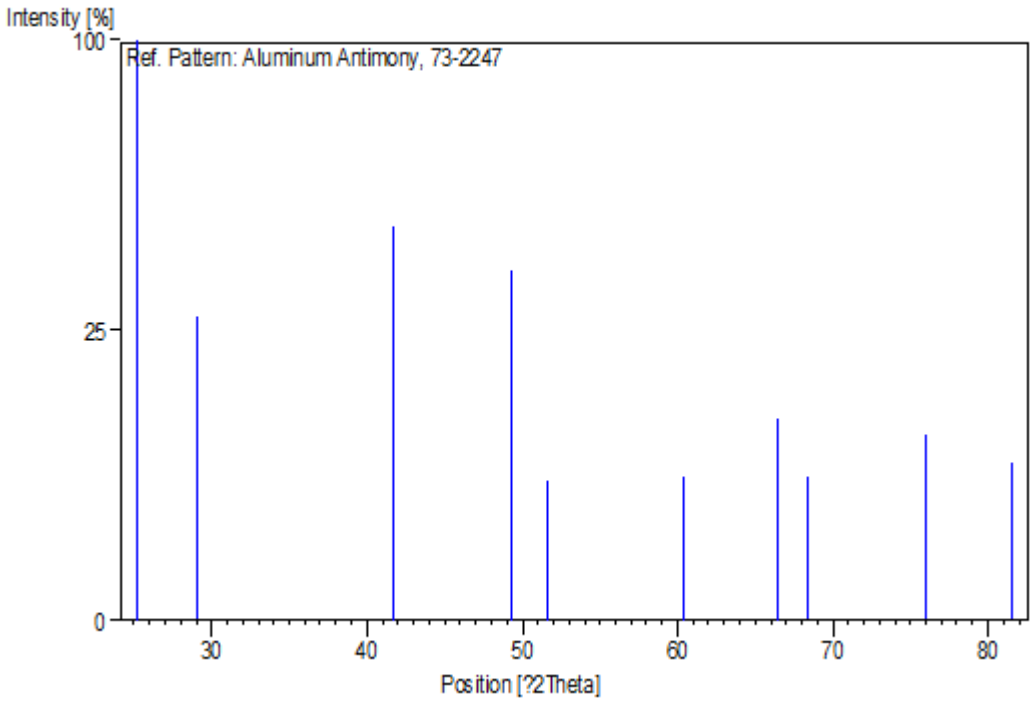
Primary reference: ***Calculated from ICSD using POWD-12++*, (1997)**

Structure: **Owen, E.A., Preston, G.D., *Proc. Phys. Soc., London*, 36**, 341, (1924)

Peak list

No.	h	k	l	d [A]	I [%]
1	1	1	1	3.53685	100.0
2	2	0	0	3.06300	27.6
3	2	2	0	2.16587	46.2
4	3	1	1	1.84706	36.2
5	2	2	2	1.76842	5.8
6	4	0	0	1.53150	6.2
7	3	3	1	1.40540	12.0
8	4	2	0	1.36982	6.1
9	4	2	2	1.25046	10.3
10	5	1	1	1.17895	7.4

Stick Pattern



7. SnO_2, JCPDS file number 77-0452

Name and formula

Reference code:	77-0452
Mineral name:	Cassiterite, syn
ICSD name:	Tin Oxide
Empirical formula:	O_2Sn
Chemical formula:	SnO_2

Crystallographic parameters

Crystal system:	Tetragonal
Space group:	P42/mnm
Space group number:	136
a (Å):	4.7552
b (Å):	4.7552
c (Å):	3.1992
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	90.0000
Calculated density:	6.92
Volume of cell:	72.34
Z:	2.00
RIR:	9.52

Subfiles and Quality

Subfiles:	Inorganic
	Mineral
	Alloy, metal or intermetalic
	Corrosion
	Modelled additional pattern
Quality:	Calculated (C)

Comments

ICSD collection code: 039178

References

Primary reference: *Calculated from ICSD using POWD-12++*, (1997)

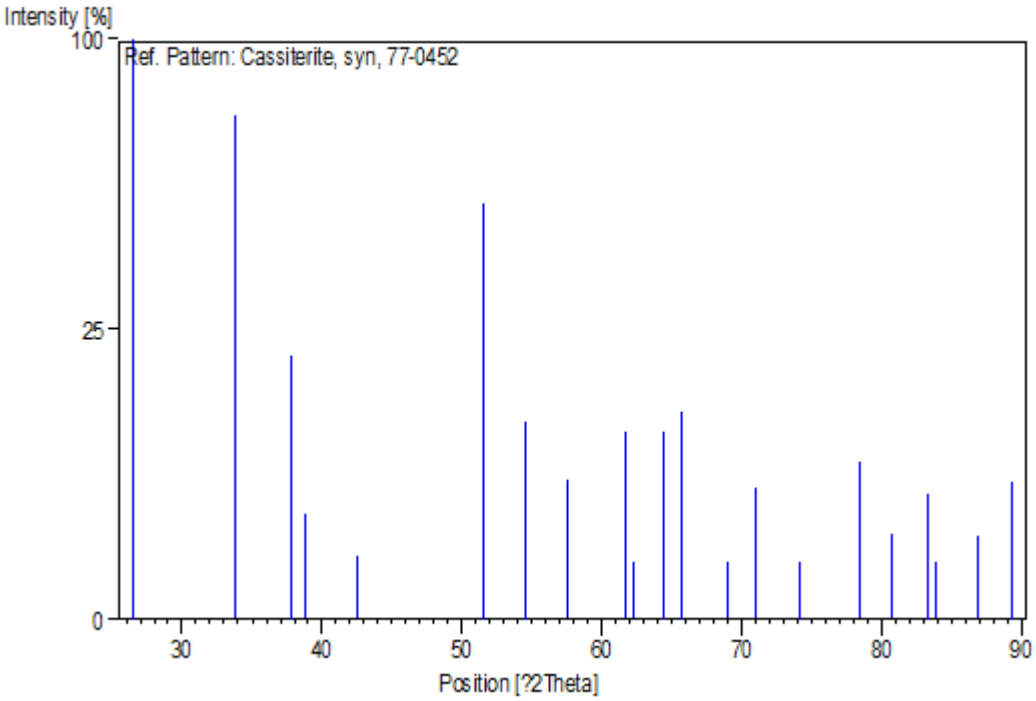
Structure: Seki, H., Ishizawa, N., Mizutani, N., Kato, M., *Yogyo Kyokaishi (J. Ceram. Assoc. Jpn.)*, **92**, 219, (1984)

Peak list

No.	h	k	l	d [A]	I [%]
1	1	1	0	3.36243	100.0
2	1	0	1	2.65438	75.8
3	2	0	0	2.37760	20.7
4	1	1	1	2.31773	3.3
5	2	1	0	2.12659	1.2
6	2	1	1	1.77101	51.6
7	2	2	0	1.68122	11.6
8	0	0	2	1.59960	5.8
9	3	1	0	1.50373	10.4
10	2	2	1	1.48823	0.1
11	1	1	2	1.44448	10.6
12	3	0	1	1.42030	12.7
13	3	1	1	1.36089	0.1
14	2	0	2	1.32719	5.1
15	2	1	2	1.27833	0.2
16	3	2	1	1.21931	7.3
17	4	0	0	1.18880	2.2
18	2	2	2	1.15887	4.7
19	4	1	0	1.15331	0.2

20	3	3	0	1.12081	2.1
21	3	1	2	1.09562	5.6

Stick Pattern



8. ZnO, JCPDS file number 89-0511

Name and formula

Reference code: 89-0511

ICSD name: Zinc Oxide

Empirical formula: OZn

Chemical formula: ZnO

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P63mc
Space group number:	186
a (Å):	3.2490
b (Å):	3.2490
c (Å):	5.2052
Alpha (degree):	90.0000
Beta (degree):	90.0000
Gamma (degree):	120.0000
Calculated density:	5.68
Volume of cell:	47.58
Z:	2.00
RIR:	5.37

Subfiles and Quality

Subfiles:	Inorganic
	Alloy, metal or intermetalic
	Corrosion
	Modelled additional pattern
Quality:	Calculated (C)

Comments

ICSD collection code:	082029

References

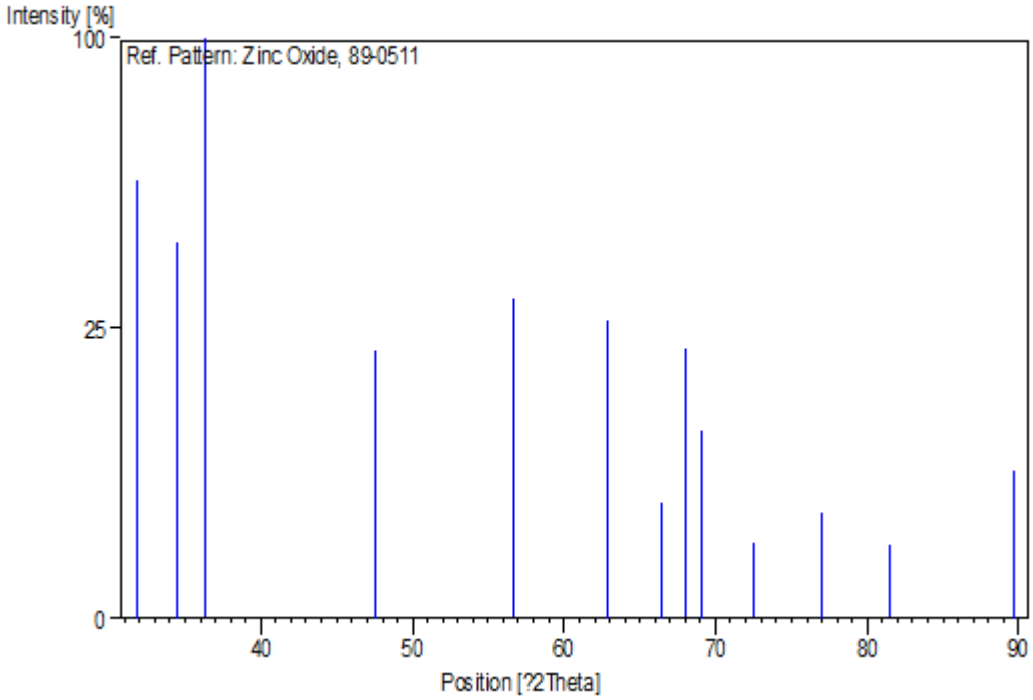
Primary reference: *Calculated from ICSD using POWD-12++*

Structure: Sawada, H., Wang, R., Sleight, A.W., *J. Solid State Chem.*, **122**, 148, (1996)

Peak list

No.	h	k	l	d [A]	I [%]
1	1	0	0	2.81372	57.4
2	0	0	2	2.60260	41.8
3	1	0	1	2.47523	100.0
4	1	0	2	1.91060	21.3
5	1	1	0	1.62450	30.5
6	1	0	3	1.47685	26.4
7	2	0	0	1.40686	4.0
8	1	1	2	1.37808	21.6
9	2	0	1	1.35813	10.6
10	0	0	4	1.30130	1.7
11	2	0	2	1.23761	3.3
12	1	0	4	1.18110	1.6
13	2	0	3	1.09277	6.5

Stick Pattern



APPENDIX B

Camera constant used for the indexing of SAED pattern

Table appendix B1. TEM constant (Lλ) at 200 kV

L (cm)	D_{111}Au (mm)	r_{111}Au (mm)	D_{111}Auv (A)	Lλ (mm.A)
40	8.70	4.35	2.355	10.2442
60	13.2	6.60	2.355	15.5430
80	17.2	8.60	2.355	20.2530
100	21.2	10.60	2.355	24.9630
120	25.2	12.60	2.355	29.6730
150	31.5	15.75	2.355	37.0912
200	41.5	20.75	2.355	48.8662
250	51.8	25.90	2.355	60.9945

APPENDIX C

Diagram of solar simulator equipments

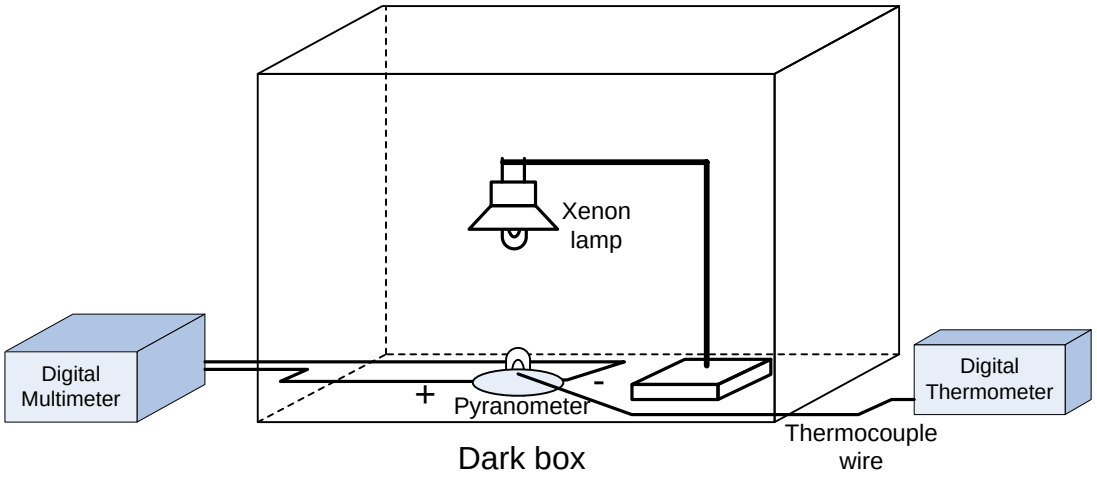


Figure C1 Diagram of solar simulator equipment calibration.

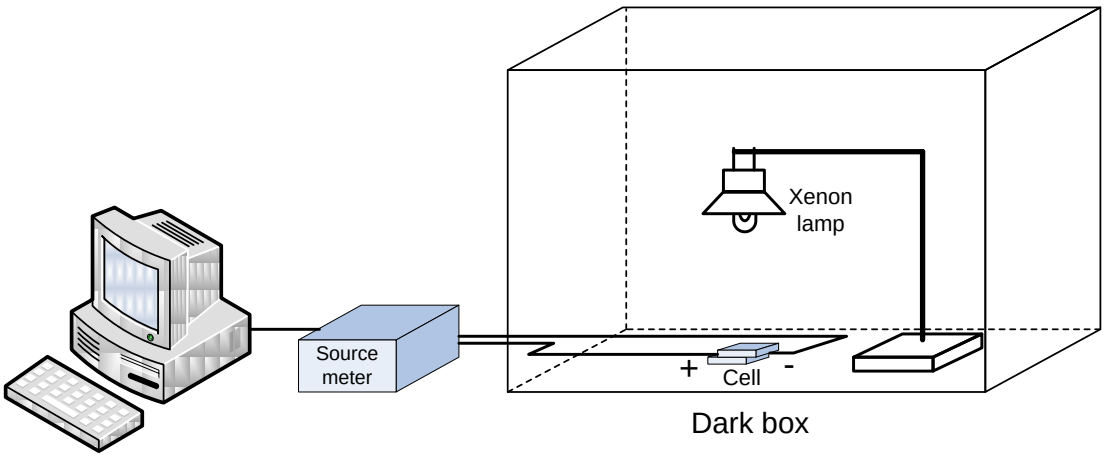


Figure C2 Diagram of solar simulator equipment.

APPENDIX D

International publications

Materials Letters 63 (2009) 2409–2412

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Transient solid-state production of nanostructured CuS flowers

Somchai Thongtem [a,*], Chaned Wichasilp [a], Titipun Thongtem [b]

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X-ray techniques
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Luminescence

ABSTRACT

CuS (hcp) with different morphologies was produced using a transient solid-state reaction by the direct flow of electricity through solids, containing 1:1 molar ratio of Cu:S powders, in a high vacuum system for different lengths of time. X-ray diffraction (XRD), selected area electron diffraction (SAED), and scanning and transmission electron microscopies (SEM and TEM) specified that the products were nanostructured CuS flowers, and nanostructured CuS composing of nanoparticles with different orientations, controlled by the length of time. Raman vibrations were detected at 474.5 cm^{-1}, and photoluminescent (PL) emissions at 347.5 nm. Both the XRD and SAED patterns are in accordance with those obtained by the corresponding simulations.

1. Introduction

Copper sulfides are the IB-VIA compounds having different phases, such as covellite (CuS), anilite (Cu_7S_4), digenite ($Cu_{1.8}S$), djurleite ($Cu_{31}S_{16}$) and chalcocite (Cu_2S) [1]. CuS is one of semiconducting materials, which have a wide variety of applications: solar radiation absorbers [2], optical filters [3] and cathode materials in lithium rechargeable batteries [2]. It has semiconducting or metallic conducting property, and transforms into a superconductor at 1.6 K [4]. There are different methods used to produce this compound: hydrothermal and solvothermal synthesis [2,5], microwave radiation [6], a polyol route [7] and solid-state reaction [8]. To the best of our knowledge, there have been no reports on the production of CuS by a transient solid-state method. Thus, it is very interesting to produce nanostructured CuS flowers, and nanostructured CuS of nanoparticles with different orientations by direct flowing of electricity through a copper–sulfur solid mixture in vacuum. This method is novel, efficient and rapid.

2. Experiment

To produce CuS (hcp), 1:1 molar ratio of Cu:S (2 g dried powders each) was put in a bottle, mixed by rotation for 1 h at ambient temperature, loaded to fill a silica tube (11 mm I.D.×10 mm long), and connected with two electrical stainless steel electrodes in a tightly closed chamber. Evacuation was done for removal of air to be 2×10^{-2} mbar absolute pressure, and argon was gradually fed into the chamber for replacement. Subsequently, argon in this chamber was evacuated to a constant absolute pressure of 2×10^{-4} mbar. To produce copper sulfide at the rapid rate, each solid mixture was heated by the direct flow of electricity (25 DC V and 20 A) through it for 1 s, 3 s, 5 s and 3 min, and left to cool down in the vacuum to room temperature. There are two reasons to use the current of 20 A for the present process. (a) The limitation of DC power supply, which was set for working at 20–200 A. The minimum current of 20 A was chosen, such that the formation process was long enough to be measured by the processing intervals. (b) The electrical property of the samples, which were measured to be 1–2 Ω or 400–800 W. These powers were high enough to produce the sulfide. Thus it is not necessary to use a higher current. Contrarily, the processing time will be longer when the electrical current is less than 20 A. A schematic diagram of the apparatus is shown in Fig. 1. For the 1 s, 3 s, and 5 s heating samples, the powders were filled with the silica tubes without the use of a compressive force (CPF). But for the 3 min heating sample, the 10^3 kg CPF was used to press the powder for 1 min. Finally, the products were intensively characterized to determine their phase, morphologies, vibrations and emissions.

3. Results and discussion

XRD spectra (Fig. 2a) of the products produced for different lengths of time were specified that they are covellite CuS of JCPDS database (reference code: 06-0464) [1]. No other characteristic peaks of impurities, such as CuO and Cu_2S, were detected. For 1 s heating, the spectrum was rather broad. Peaks at $2\theta = 31.8–32.9°$ were merged into a single one, showing that the product was composed of nanosized particles with low degree of crystallinity. The spectra became sharper and narrower when the length of time was longer, and the single

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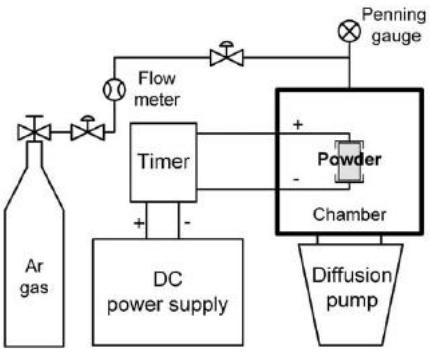

Fig. 1. A schematic diagram of the apparatus used for the production of covellite CuS.

broad peak split into two peaks — the (103) and (006) at 31.8° and 32.9°, respectively. For 3 min heating, the spectrum was the sharpest. At this stage, atoms were in lattice order and formed nanostructured CuS with the highest degree of crystallinity. The prolonged time has the influence on the phase formation by assisting Cu and S atoms in violent vibrating and diffusing at longer time. These atoms have more chance to reside in their normal lattices. The present research gives the yields of 87.9, 85.0, 84.6 and 95.1 wt.% for the 1 s, 3 s, 5 s and 3 min heating, respectively.

Fig. 2b shows the simulated XRD spectra [9] of the 3 s and 5 s products, and was used to specify that the experimental spectra could exist in reality. The 2θ Bragg's angles and intensities of different crystallographic planes from the experiment, simulation and JCPDS database [1] are in good accordance. Some peaks of the JCPDS database were not detected in the experiment and simulation, due to their low intensity values.

SEM, TEM and HRTEM images (Figs. 3 and 4) show different stages for the formation of nanostructured CuS flowers. For 1 s long, the product (Figs. 3a and 4a) was nanostructured CuS, composing of a number of nanosized particles with different orientations. Then it transformed into the 1–2 μm nanostructured flowers by increasing the length of time — incomplete (Fig. 4b) and complete (Fig. 4c and d) flowers for 3 s and 5 s, respectively. At these stages, several plates (Figs. 3b, and 4b–d) combined together to form a flower. For 5 s long, a

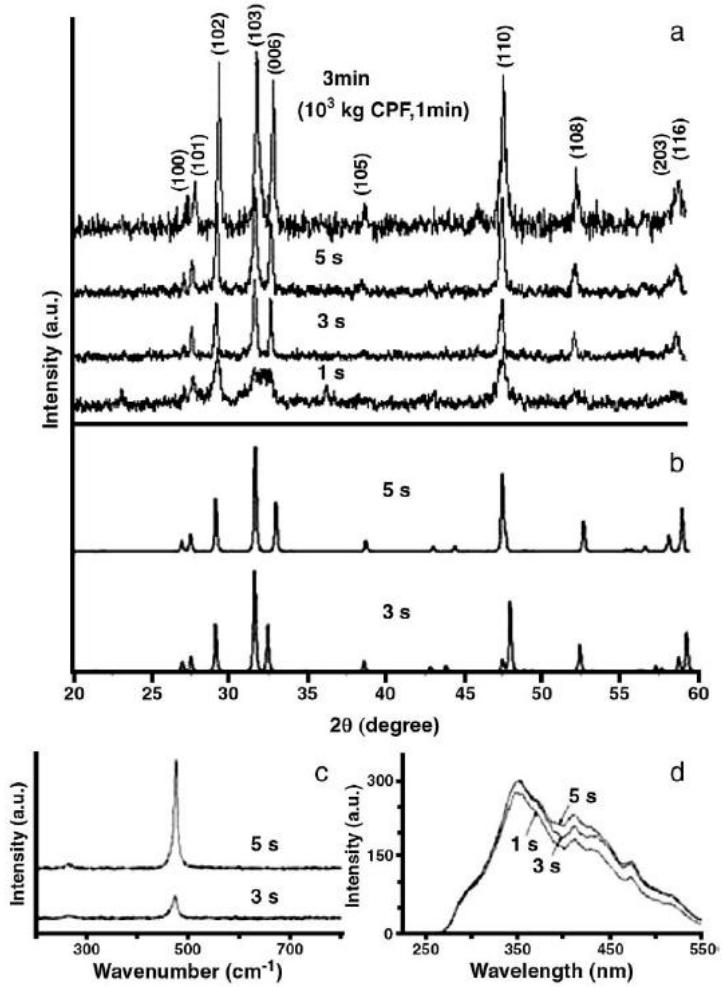

Fig. 2. (a) XRD, (b) simulated, (c) Raman and (d) PL spectra of the products produced under different lengths of time.

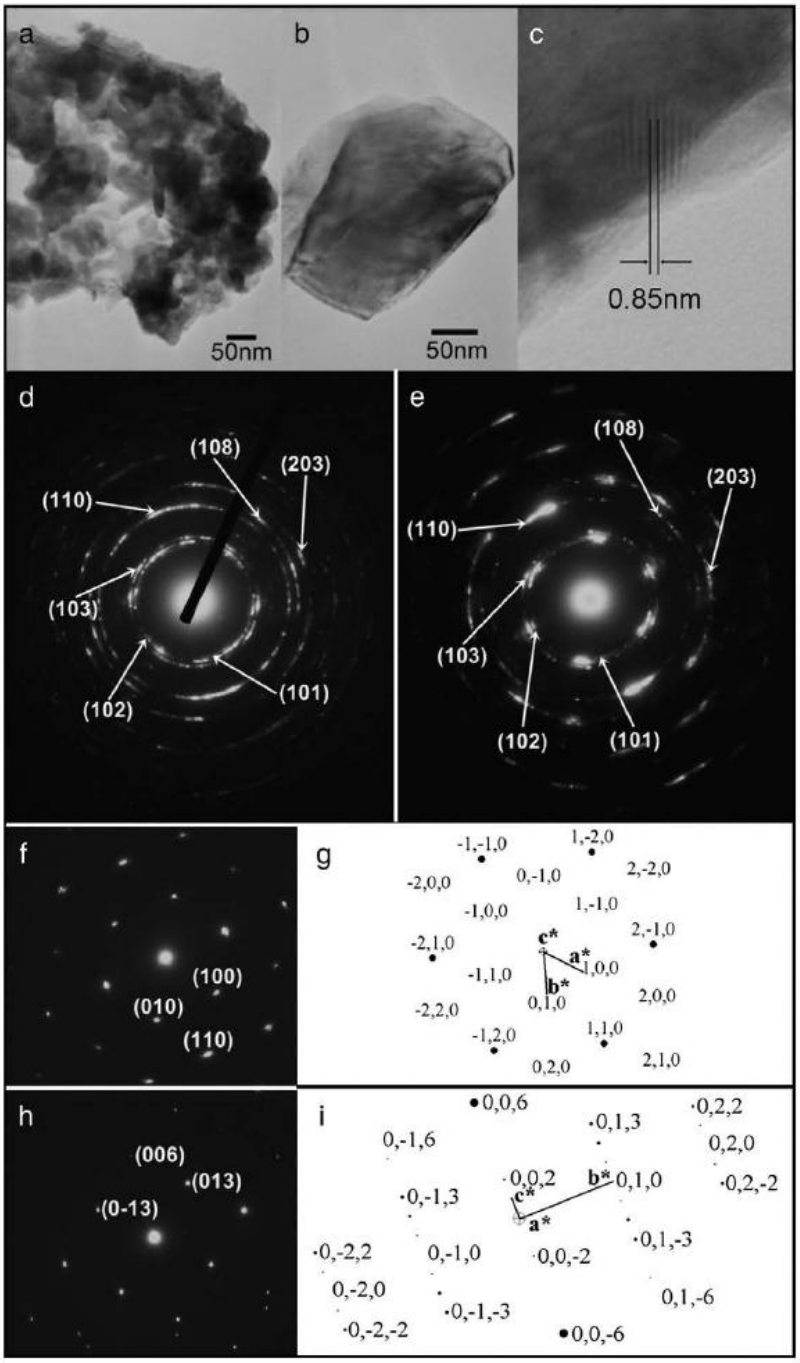

Fig. 3. TEM and HRTEM images, and SAED patterns of CuS produced for 1 s (a), 3 s (d), and 5 s (b, c, e, f and h). (g and i) are the simulated patterns of (f and h), respectively.

set of parallel crystallographic planes (Fig. 3c) with 0.85 nm space were detected. They are the (002) plane of covellite CuS phase [1], showing that these flowers are the best crystalline in nature. Electrical energy was directly supplied to the system composing of Cu and S powders to accelerate CuS (hcp) formation in vacuum. The length of time has very strong influence on the product morphologies and crystallinities.

Fig. 3d and e shows SAED patterns of polycrystalline products produced for 3 s and 5 s, respectively. These diffraction patterns were composed of several concentric rings, corresponding to the planes of polycrystalline CuS with hexagonal structure of the JCPDS database [1]. SAED patterns (Fig. 3f and h) of single crystals with two different orientations were indexed [10], and specified as hexagonal CuS [1] with the [001] and [−100] directions as the zone axes, respectively.

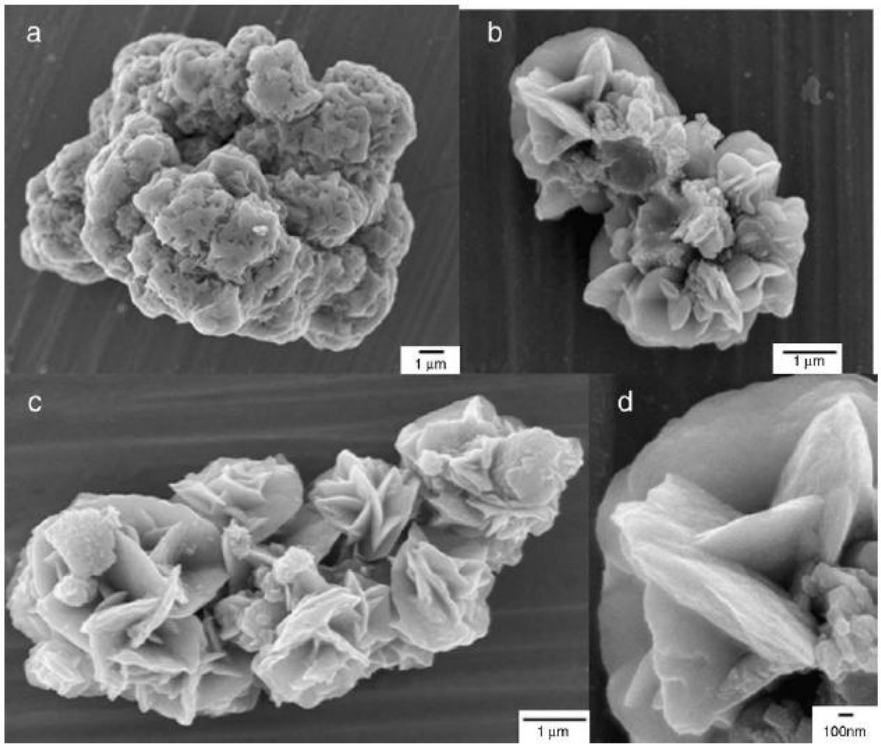

Fig. 4. SEM images of CuS produced for (a) 1 s, (b) 3 s, and (c and d) 5 s.

Simulated electron diffraction patterns [9] (Fig. 3g and i) corresponded very well with those obtained by the interpretation (Fig. 3f and h).

Raman spectra (Fig. 2c) of CuS produced for 3 s and 5 s show that the vibration modes are in the same wavenumber at 474.5 cm^{-1}, corresponding to lattice vibrations [11]. The present results are in accordance with those characterized by Minceva-Sukarova et al. as a strong and sharp peak of CuS film at 474 cm^{-1} [11], and by Wang et al. of nanocrystalline CuS film with the size of 21.5 nm at 474 cm^{-1} [12]. It is worth noting that crystalline degree of the products has the influence on the peak intensity as well. For the 5 s product, its intensity is the strongest.

PL emissions of solid CuS (Fig. 2d) were determined using a 202 nm excitation wavelength at room temperature. These emissions are at the same values of 347.5 nm with their shoulders at 410.5 nm and 472 nm. Comparing to the emission of CuS nanoplates at 339 nm determined by Zhang and Zhang [2], the present results are red-shift, caused by the morphological difference [13]. PL intensities were increased with the increase in the length of time. For the 5 s product, it is the best crystal and its PL intensity is the highest.

4. Conclusions

Nanostructured CuS flowers and nanostructured CuS composing of nanoparticles with different orientations were successfully produced from a 1:1 molar ratio of Cu:S powders using a transient solid-state method, by the direct flow of DC current through the solids. The phase and morphologies were clearly detected. Their vibrations were at 474.5 cm^{-1}, and photoluminescence at 347.5 nm. The complete flower-structured CuS, produced for 5 s, was the best crystal. Its Raman and PL intensities were at the highest. A number of the (002) crystallographic planes were detected on its petal.

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Electric field assisted processing and characterization of AlSb nanocrystals

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ABSTRACT

AlSb nanocrystals were produced by the direct flow of electrons through powder mixture of 1:1 M ratio Al:Sb. The phase, morphology, and vibration modes were characterized using XRD, TEM, and Raman spectroscopy. The optical property was also investigated using UV-Vis-NIR spectrophotometry. In the present research, the products were pure AlSb nanocrystals at 80 A for 10 min, and 110 A for 3 s, with the indirect energy band gaps of 1.647 eV and 1.688 eV, respectively.

1. Introduction

Recently, III–V nanostructured materials are very attractive for a number of applications in science and technology. One of them is AlSb, which has wide variety applications – photovoltaic cells, p–n junction diodes, and anodes for Li-ion batteries [1]. It is zinc-blende structure with a lattice constant of 0.6126 nm [2,3], and high melting point (1058 °C) [4]. It shows sharp-line donor-acceptor pair spectrum, caused by electron-hole transition process [2]. AlSb is able to use as anodes for lithium-ion batteries – both Al and Sb are active in forming alloys with lithium [5]. Generally, AlSb is the p-type intrinsic semiconductor. By doping with Se, Te and S as donors, it transforms into the n-type extrinsic one [1]. When it was deposited on a Si (001) wafer, it nucleated as the crystalline quantum dots, and formed as defect-free buffers on lattice mismatched substrates [6]. In this research, AlSb nanocrystals were produced by the direct flow of electrons through solid mixtures, and further characterized. This process is novel, fast, effective, and environmentally benign.

2. Experiment

To produce AlSb nanocrystals, 1:1 M ratio of Al:Sb (total weight of 2 g dried powder) was put in a bottle, mixed by rotation for 1 h at room temperature. The 1 ton force was used to press the powder for 1 min to form a disk, which was connected with two electrical stainless steel electrodes in a tightly closed chamber (Fig. 1). Evacuation was done to achieve 3×10^{-4} mbar absolute pressure. Then each disk was heated by the direct flow of current using 25 DC V, under different conditions: C1 (80 A, 5 min), C2 (80 A, 10 min), C3 (110 A, 2 s) and C4 (110 A, 3 s), and left to cool down to room temperature. The phase, morphology, vibration modes, and optical property were further characterized.

3. Results and discussion

XRD spectra (Fig. 2) of AlSb, produced by the direct flow of 80 A and 110 A currents through the solid mixtures for different lengths of times, were compared with the JCPDS database [3]. For C1 and C3 conditions, the products were cubic AlSb (JCPDS no. 73-2247) containing some Al and Sb impurities (JCPDS nos. 01-1176 for Al, and 02-0587 and 02-0592 for Sb). At these stages, the chemical reactions of Al and Sb are still incomplete. Upon processing at the C2 and C4 conditions, the products were pure AlSb without any impurity detection. Al and Sb completely combined together to form AlSb with cubic crystal system ($a = b = c = 6.1260$ Å) [3].

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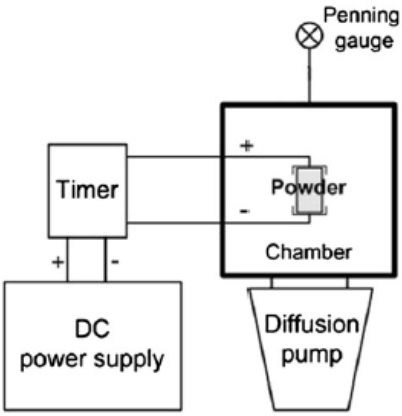

Fig. 1. Schematic diagram for the production of AlSb by the direct flow of current through the solid mixtures.

Comparing between the C2 and C4 conditions, the latter produced better crystalline than the former. During the direct flow of current through the solids, some Al and Sb could evaporate as well.

Raman spectra (Fig. 3) show three Raman shifts at 113.3, 145.9, and 320.2 cm^{-1}, for AlSb produced at the C2 and C4 conditions. The 1st, 2nd and 3rd Raman shifts correspond very well with those characterized by Azuhata et al. – specified as the 2 TA(L), 2 TA(X) and TO(Γ) modes [7], respectively. No detection of any impurity peaks in these products – agree very well with the above XRD analysis. But for those produced at the C1 and C3 conditions, additional peaks at 251.9 cm^{-1} were detected. They correspond with the Raman shift of antimony, specified by RRUFF [8]. Comparing to 30 mW He–Ne laser with 632.8 nm (red) wavelength, a great deal of energy was lost during the Raman analysis, caused by the inelastic scattering process.

SAED patterns (Fig. 4) of AlSb produced at the C2 and C4 conditions were indexed and interpreted [9]. Fig. 4a and d shows several concentric rings of diffraction spots of transmitted electrons through a number of polynanocrystals with different orientations [10–13]. Fig. 4b and e shows two SAED patterns of single crystal [12–14], and the electron beams in the $[\bar{5}36]$ and $[\bar{1}1\bar{1}]$ directions, respectively. All these four patterns were proved that the products are cubic AlSb [3]. Diffraction patterns for AlSb with electron beams in the $[\bar{5}36]$ and $[\bar{1}1\bar{1}]$ directions were also simulated [15], and are

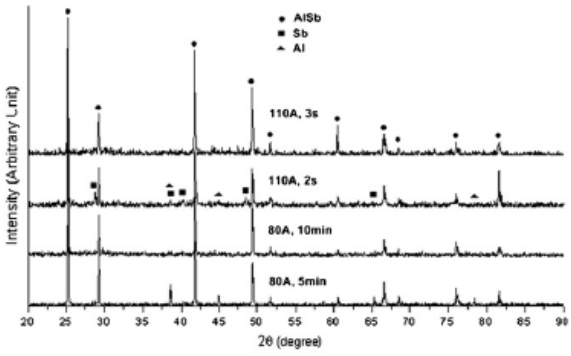

Fig. 2. XRD spectra of AlSb produced under different conditions.

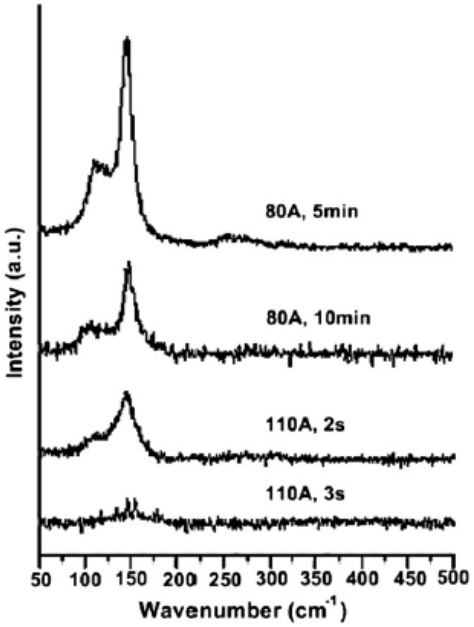

Fig. 3. Raman spectra of AlSb produced under different conditions.

shown in Fig. 5. They are in symmetric and systematic order, with the a^*, b^* and c^* reciprocal lattice vectors for both patterns in the [100], [010], and [001] directions. For one crystal structure, the corresponding reciprocal lattice vectors are the same although the electron beams are different. Comparing between the corresponding SAED and simulated patterns, they are in good accordance. Typical examples of TEM images (Fig. 4c and f) of AlSb produced at the C2 and C4 conditions showed that these products were composed of a number of nanograins with different orientations – 50 nm and 20 nm in sizes, respectively. The XRD and SAED analyses proved that these nanograins were crystalline in nature.

Absorption spectra of AlSb produced at the C2 and C4 conditions were characterized using UV-Vis-NIR spectrophotometer with the aid of the following equations [16,17].

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g), \tag{1}$$

$$\alpha = -(\log T)/t, \tag{2}$$

$$t = bC/\rho, \tag{3}$$

where α is the total absorption coefficient, $h\nu$ the photon energy, B a constant, E_g the indirect energy gap, T the transmittance of photon through the suspension in ethanol (concentration, $C = 0.001$ g/cm^3) containing in the cuvettes (spectroscopy cells) with the path length (b) of 10.00 mm, t the effective thickness, and ρ the density of AlSb. The curves of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for indirect allowed transition were plotted (Fig. 6), and extrapolated to $\alpha = 0$. The absorption edge energies, corresponding to the energy gaps of AlSb produced at the C2 and C4 conditions, were respectively determined [16] to be 1.647 eV and 1.688 eV, controlled by particle-sizes – energy gap increases with the decreasing in size [18] of AlSb particles. These values are in accordance with the indirect optical interband transition of AlSb reported by the research teams of Misra [1], Al-Douri [19], Anani [20], and Vurgaftman [21].

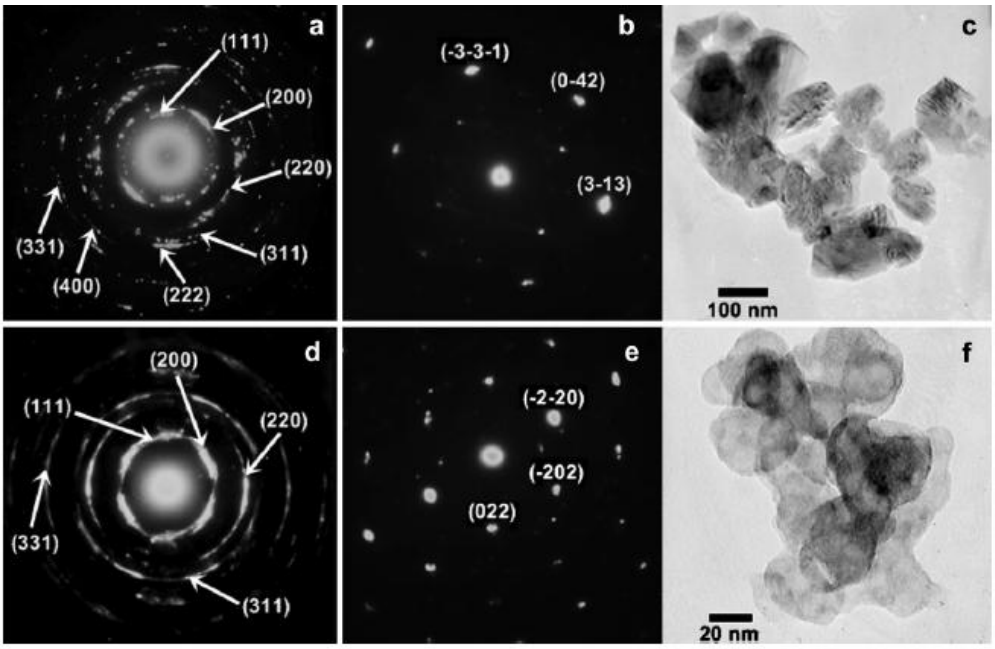

Fig. 4. SAED patterns and TEM images of AlSb produced at (a–c) C2, and (d–f) C4 conditions.

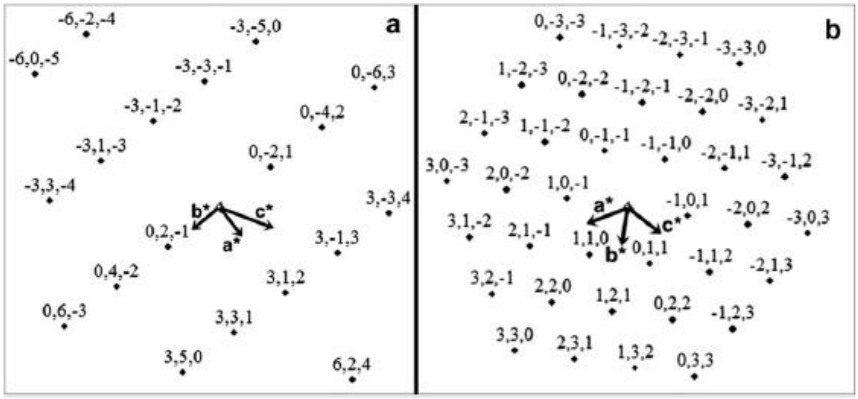

Fig. 5. (a, b) The simulated patterns of Fig. 4b and e, respectively.

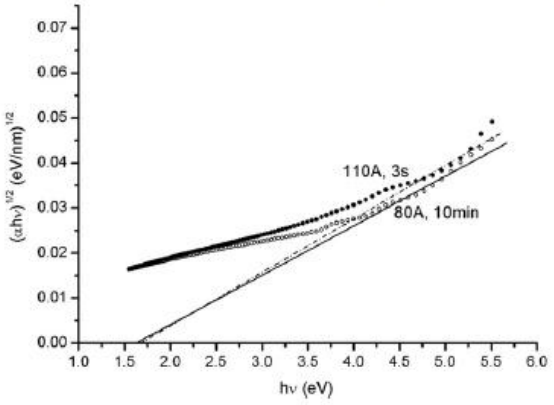

Fig. 6. The relationship between $(\alpha h\nu)^{1/2}$ and $h\nu$ of AlSb nanocrystals produced at the C2 and C4 conditions.

4. Conclusions

Pure AlSb nanocrystals were successfully produced by the direct flow of electrons through solid mixtures – the novel, fast, effective, and environmentally benign process. The phase and nanocrystals were clearly detected, including three Raman shifts at 113.3, 145.9, and 320.2 cm^{-1}. Indirect energy band gaps are 1.647 eV and 1.688 eV, for AlSb nanocrystals with the sizes of 50 nm and 20 nm, respectively.

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Publications

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2. Somchai Thongtem, Chaned Wichasilp, Titipun Thongtem ”Transient Solid-State production of nanostructured CuS flowers” Materials Letters 2009 ; 63 : 2409-2412.

3. Chaned Wichasilp, Watcharachai Wiriyasuttiwong, Kajornsak Kantapanit "Design of Fuzzy Logic Controllers by Fuzzy c-Means Clustering " Thammasat International Journal Science and Technology, Vol.8, No.2, pp. 12-16, April-June 2003.

4. Chaned Wichasilp, Watcharachai Wiriyasuttiwong, Vasutan Tunbunheng, Kajornsak Kantapanit "Fuzzy C-Means Clustering Designed FLC for Air-Conditioning System" Engineering Journal of Siam University, Vol.7, No.4 ,pp.23-27 Jan – June 2002.

International Conference Participations

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