

Solid-State Synthesis

Inorganic Halides
for Scintillation

Superconductors

Piezoelectric Crystals

Solid-State Metathesis
Materials Synthesis

Solvothermal Routes
to Nanomaterials

Intermetallic Compounds
of Antimony and Bismuth

Introduction

Welcome to the Sigma-Aldrich technical guide for solid-state synthesis. In this guide, you will find a sampling of our broad product portfolio and short reviews from researchers in relevant technical fields. At Sigma-Aldrich, our mission is to inspire and advance your research. I hope these tools will inspire innovative solutions to the unique challenges inherent in solid-state synthesis.

Solid-state synthesis is a bit of a misnomer. Often the interaction of the component materials occurs not in the solid state but in a molten flux or a rapidly condensing vapor phase. The term solid-state synthesis is often used to describe interactions where neither a solvent medium nor controlled vapor-phase interactions are utilized. Since these reactions often involve extreme conditions (high temperature and/or high pressure), solvothermal techniques are considered part of the solid-state tool kit. Ultimately, solid-state synthesis is used where other techniques will not suffice: the production of bulk crystals, refractory ceramics, solid solutions, and glasses. Solid-state synthesis is used to create the unique compositions and morphologies needed to generate the desired attributes in scintillation crystals, piezoelectrics, and other advanced materials. Sigma-Aldrich is proud to contribute to the field of solid-state synthesis for advanced applications.

Included in this brochure is a small sampling of our broad product portfolio of solid-state synthesis materials. Visit us at sigma-aldrich.com/matsci for our complete line of products for solid-state synthesis.

I would like to thank our contributors in this technical guide for their reviews: Dr. Kevin Zawiski, BAE Systems; Dr. Richard Blair, Jet Propulsion Laboratory and Prof. Richard Kaner, UCLA; Prof. Arthur Mar, University of Alberta; and Prof. Bonnie Gersten, CUNY, Queens College.

Sincerely,



Luke Grocholl, Ph.D.
Materials Science Team
Sigma-Aldrich Corporation



Sigma-Aldrich Quality

Quality Assurance

Quality Control and Quality Assurance are an integral part of every Sigma-Aldrich product. We preserve our tradition of uncompromising quality by bringing to bear our full array of resources on the products we offer. Sigma-Aldrich's quality control laboratories are well equipped to safely handle and thoroughly characterize chemicals that span our broad spectrum of product lines. Our QC/QA team of over 100 chemists and technicians at our manufacturing sites in USA and Europe analyze all Sigma-Aldrich products. Assays range from simple solubility and melting point determinations to various titrations and XRD. Our new ICP-mass spectrometer (ICP-MS) can detect trace metals to parts per billion (ppb) level.



Robert Voight of the Sigma-Aldrich Quality Control team with one of our ICP-MS spectrometers.

Solid-State Synthesis for Advanced Applications



For more information, visit
sigma-aldrich.com/matsci

"Nines Purity"

For elements and metal-containing compounds, it is common practice to refer to "purity" as the determined trace metallic impurities (TMI, typically determined by ICP spectroscopy) subtracted from 100%. By convention, the "nines" purity indicates an acceptable purity range. For example, "five-nines" (99.999%) indicates a TMI of up to 20 ppm may be present in a lot. Any "nines" purity followed by a "+" dictates a specific upper limit on the total allowable metallic impurities. For example, a material listed as "99.999+%" contains less than 10 ppm metallic impurities.

Certificates of Analysis

As a service to our customers, we provide batch-specific trace metals analysis indicating all detected metallic impurities for materials with purities of 99.9% or greater. In addition, we report the chemical assay for each lot of high purity compounds. Chemical assay is determined by classical methods and may not correspond to the spectrographic purity due to such factors as absorption of moisture or atmospheric gases, product nonstoichiometry, or limited precision of assay techniques.

The purity of rare-earth (Z = 39 and 57-71) products is relative to other rare-earth elements only. Unavoidable contamination from reducing agents or crucible materials, which may account for as much as several percent, is not included in purity statements. Due to the extreme difficulty in isolating the pure metal, hafnium products may contain up to 5% zirconium contamination that is not reported in purity statements.

TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit sigma-aldrich.com/matsci.

Sigma-Aldrich Center of Excellence Materials for Solid-State Synthesis



Our Urbana, Illinois R&D and manufacturing facility has a proven track record of providing you, our valued customer, with the ultra-high purity source materials required to accelerate your science.

Capabilities

- Dedicated R&D with extensive experience in solid-state synthesis
- Proprietary technology for beaded material manufacture
- Reactive gas and high-temperature (1000+ °C) techniques
- Metal distillation and materials sublimation for purification
- Internal glass shop with extensive quartz expertise
- Crystal scrap reprocessing

Quality Assurance

- Sophisticated analytical capabilities including ICP-MS
- Materials sealed in ampoules using argon atmosphere glove box conditions
- Dedicated dry room for hygroscopic salts

Advantages of Proprietary Beaded Materials

- Increased crucible loading
- Reduced static buildup
- Dust free
- Reduce surface area: minimized moisture adsorption

New Products for
Solid-State Synthesis

NEW Products for Solid-State Synthesis

Barium fluoride, precipitated, 99.999%

BaF₂
MW: 175.34
[7787-32-8]
MP: 354 °C
BP: 2260 °C
4.89 g/mL at 25 °C

652458-25G	25 g
652458-100G	100 g

Bismuth(III) bromide, 99.999%

BiBr₃
MW: 448.69
[7787-58-8]
MP: 219 °C
BP: 462 °C
5.7 g/mL at 25 °C

654981-1G	1 g
654981-5G	5 g

Copper(I) chloride, anhydrous, beads, 99.99+%

CuCl
MW: 99.00
[7758-89-6]
MP: 430 °C
BP: 1490 °C
4.14 g/mL at 25 °C

651745-5G	5 g
651745-25G	25 g

Copper(I) oxide, anhydrous, powder, 99.99+%

Cu₂O
MW: 143.08
[1317-39-1]
MP: 1320 °C
BP: 1800 °C
6.00 g/mL at 25 °C

566284-5G	5 g
566284-25G	25 g

Dysprosium(II) iodide, anhydrous, powder, 99.9+%

DyI₂
MW: 416.31
[36377-94-3]
MP: 721 °C

652423-1G	1 g
652423-5G	5 g

Holmium(III) phosphate, anhydrous, powder, 99.99+%

HoPO₄
MW: 259.90
[14298-39-6]

641677-1G	1 g
641677-5G	5 g

For questions, product data, or new product suggestions,
please contact the Materials Science Team: matsci@sial.com.

Order: 1.800.325.3010 Technical Service: 1.800.231.8327

 ALDRICH®

Lanthanum(III) bromide, anhydrous, powder, 99.99+%

LaBr₃
 MW: 378.64
 [13536-79-3]
 MP: 783 °C
 BP: 2280 °C
 5.06 g/mL at 25 °C

656119-2G	2 g
656119-10G	10 g

Lutetium(III) iodide, anhydrous, beads, -10 mesh, 99.9%

LuI₃
 MW: 555.68
 [13813-45-1]
 MP: 1050 °C
 BP: 1200 °C
 5.6 g/mL at 25 °C

649872-1G	1 g
649872-5G	5 g

Neodymium(II) iodide, anhydrous, powder, 99.9+%

NdI₂
 MW: 398.05
 [61393-36-0]
 MP: 562 °C

652431-1G	1 g
652431-5G	5 g

Neodymium(III) iodide, anhydrous, powder, 99.9%

NdI₃
 MW: 524.95
 [13813-24-6]
 MP: 784 °C

659215-1G	1 g
659215-5G	5 g

Strontium fluoride, precipitated, 99.995%

SrF₂
 MW: 125.62
 [7783-48-4]
 MP: >1400 °C
 BP: 2489 °C
 4.24 g/mL at 25 °C

652466-25G	25 g
652466-100G	100 g

Thulium(II) iodide, anhydrous, powder, 99.9+%

TmI₂
 MW: 422.74
 [60864-26-8]
 MP: 756 °C

645168-5G	5 g
645168-25G	25 g

Tungsten(VI) chloride, anhydrous, powder, 99.99+%

WCl₆
 MW: 396.57
 [13283-01-7]
 MP: 275 °C
 BP: 347 °C
 3.52 g/mL at 25 °C

653268-1G	1 g
653268-5G	5 g

Yttrium trifluoroacetate, anhydrous, powder, 99.99+%

Y(COOCF₃)₃
 MW: 427.95

659886-25G	25 g
------------	------

Zirconium(IV) chloride, anhydrous, powder, 99.99%

ZrCl₄
 MW: 233.03
 [10026-11-6]
 BP: 331 °C
 2.8 g/mL at 25 °C

647640-5G	5 g
647640-25G	25 g

Inorganic Halides for Scintillation

Luke Grocholl, Ph.D.
 Materials Science Team
 Sigma-Aldrich Corporation

The 1948 discovery by Hofstadter that sodium iodide doped with thallium exhibits extremely high light-yield and conversion efficiency launched the era of modern radiation spectrometry.¹ More than half a century later, inorganic halide salts, particularly when doped, possess some of the best characteristics of all scintillation materials.² In fact, thallium-doped sodium iodide still exhibits the highest conversion efficiency of any known scintillation material.

Rare-Earth Halides

Doped lanthanide halides are a promising new class of scintillation crystals. Recent papers³⁻⁵ show that these materials possess not only high light output, but also the proportionality necessary for high-energy resolution. In addition, doped lanthanide halides exhibit fast response times and good γ -ray stopping efficiency. High-purity, anhydrous lanthanide halide source materials are expensive and difficult to obtain in the quantities necessary for bulk crystal growth. Sigma-Aldrich holds a unique position as a supplier of ultra-dry rare-earth salts in bulk quantities.

Inorganic halide crystals represent the benchmark in scintillator materials. They continue to meet material challenges through active research and development. Essential to the growth of these crystals are ultra-high purity, anhydrous source materials. Proprietary Sigma-Aldrich technology is used to produce beaded materials whose reduced surface area minimizes moisture absorption and allows increased crucible loading, boosting crystal yield. Scrap shards cut from desired crystals can be reprocessed by Sigma-Aldrich to provide pristine materials, thus increasing the economic efficiency of scintillation crystal growth. Precursor materials must also be free of significant amounts of trace radioactive impurities. Sigma-Aldrich has a center of excellence for high quality source materials, as well as technical knowledge and commitment, necessary to advance your high technology applications.

References

- (1) Hofstadter, R. *Phys. Rev.* **1948**, *74*, 100.
- (2) Derenzo, S. E. et al. *Nuc. Instrum. Methods* **2002**, *505*, 111.
- (3) Guillot-Noël, O. et al. *J. Lumin.* **1999**, *85*, 21.
- (4) van Loef, E. V. D. et al. *Appl. Phys. Lett.* **2000**, *77*, 1467.
- (5) van Loef, E. V. D. et al. *Phys. Res. A* **2003**, *496*, 138.

**TO ORDER: Contact your local Sigma-Aldrich office (see back cover),
 call 1-800-325-3010 (USA), or visit sigma-aldrich.com/matsci.**

Halides

Name	Formula	MW	CAS	MP	BP	Density at 25 °C	Cat. No.	List Price
Barium fluoride, anhydrous, powder, 99.999%	BaF ₂	175.34	[7787-32-8]	354 °C	2260 °C	4.89 g/mL	449660-10G 449660-50G	
Bismuth(III) fluoride, 99.99+%	BiF ₃	265.98	[7787-61-3]	649 °C	900 °C	8.3 g/mL	401528-5G 401528-25G	
Calcium fluoride, anhydrous, powder, 99.99%	CaF ₂	78.08	[7789-75-5]	1418 °C	2260 °C	3.18 g/mL	449717-5G 449717-25G	
Cerium(III) fluoride, anhydrous, powder, 99.99%	CeF ₃	197.12	[7758-88-5]	1430 °C	2327 °C	6.16 g/mL	229555-2G 229555-10G 229555-50G	
Cerium(III) chloride, anhydrous beads, -10 mesh, 99.99+%	CeCl ₃	246.48	[7790-86-5]	848 °C	1730 °C	4.00 g/mL	429406-5G 429406-25G	
Cerium(III) bromide, anhydrous, beads, particle size -10 mesh, 99.99%	CeBr ₃	379.85	[14457-87-5]	730-732 °C	1705 °C	5.18 g/mL	563226-5G 563226-25G	
Cesium fluoride, 99.99%	CsF	151.90	[13400-13-0]	682 °C	1231 °C	4.115 g/mL	255718-10G 255718-50G	
Cesium iodide, anhydrous, beads, particle size -10 mesh, 99.999%	CsI	259.81	[7789-17-5]	626 °C	1280 °C	4.51 g/mL	429384-1G 429384-10G	
Europium(III) fluoride, anhydrous, powder, 99.99%	EuF ₃	208.96	[13765-25-8]	1276 °C	2500 °C		449806-1G 449806-5G	
Gadolinium(III) bromide, anhydrous, powder, 99.99%	GdBr ₃	396.98	[13818-75-2]	770 °C		4.6 g/mL	485020-2G 485020-10G	
Lanthanum(III) fluoride, anhydrous, powder, 99.99%	LaF ₃	195.91	[13709-38-1]	1493 °C	2327 °C	5.936 g/mL	449857-5G 449857-25G 449857-100G	
Lanthanum(III) chloride, anhydrous, beads, particle size -10 mesh, 99.99+%	LaCl ₃	245.27	[10099-58-8]	860 °C	1812 °C	3.84 g/mL	449830-5G 449830-25G	
Lanthanum(III) bromide, anhydrous, beads, particle size -10 mesh, 99.99+%	LaBr ₃	378.64	[13536-79-3]	783 °C	2280 °C	5.06 g/mL	449822-2G 449822-10G	
Lanthanum(III) iodide, anhydrous, beads, particle size -10 mesh, 99.9%	LaI ₃	519.62	[13813-22-4]	772 °C		5.63 g/mL	413674-1G 413674-5G	
Lead(II) iodide, beads, particle size -10 mesh, 99.999%	PbI ₂	461.01	[10101-63-0]	402 °C	2672 °C	6.16 g/mL	554359-5G 554359-25G	
Lutetium(III) chloride, anhydrous, powder, 99.99%	LuCl ₃	281.33	[10099-66-8]	279 °C	905 °C	3.98 g/mL	450960-1G 450960-5G	
Lutetium(III) bromide, anhydrous, powder, 99.99%	LuBr ₃	414.68	[14456-53-2]	1025 °C	1440 °C		587133-1G 587133-5G	
Lutetium(III) iodide, anhydrous, powder, 99.9%	LuI ₃	555.68	[13813-45-1]	1050 °C	1200 °C	5.6 g/mL	460575-1G 460575-5G	
Mercury(II) bromide, anhydrous, beads, particle size -10 mesh, 99.999%	HgBr ₂	360.41	[7789-47-1]	236 °C	318 °C	6.05 g/mL	449121-5G 449121-25G	
Mercury(II) iodide, anhydrous, beads, particle size -10 mesh, 99.999%	HgI ₂	454.40	[7774-29-0]	259 °C	322 °C	6.21 g/mL	449180-5G 449180-25G	
Praseodymium(III) chloride, anhydrous, beads, particle size -10 mesh, 99.99%	PrCl ₃	247.27	[10361-79-2]	786 °C	1710 °C	4.00 g/mL	451215-1G 451215-5G 451215-25G	
Praseodymium(III) bromide, anhydrous, powder, 99.99%	PrBr ₃	380.63	[13536-53-3]	693 °C	1547 °C	5.30 g/mL	439703-2G 439703-10G	
Sodium iodide, anhydrous, beads, particle size -10 mesh, 99.999%	NaI	149.89	[7681-82-5]	661 °C	1304 °C	3.67 g/mL	439681-5G 439681-25G	
Thallium(I) bromide, anhydrous, beads, particle size -10 mesh, 99.999%	TlBr	284.28	[7789-40-4]	>300 °C	815 °C	7.5 g/mL	336270-10G 336270-50G	
Thallium(I) iodide, anhydrous, beads, particle size -10 mesh, 99.999%	TlI	331.27	[7790-30-9]	440 °C	824 °C	7.29 g/mL	458813-10G 458813-50G	

For questions, product data, or new product suggestions,
please contact the Materials Science Team: matsci@sial.com.

Superconductors

Luke Grocholl, Ph.D.
Materials Science Team
Sigma-Aldrich Corporation

Superconductors are materials that exhibit zero electrical resistance below a certain temperature defined as the critical temperature (T_C). Prior to 1986, the highest T_C reported was 20 K for Nb_3Ge and Nb_3Sn .¹ During 1986–87, a group led by Johannes Bednorz and Karl Müller reported the ceramic oxides $La_{2-x}Ba_xCuO_{4-x}$ and $YBa_2Cu_3O_7$ (Sigma-Aldrich Cat. No. **328626**) superconduct above the boiling point of nitrogen (77 K).^{2,3} Materials whose T_C is greater than the boiling point of nitrogen (a common, readily available, cryogenic coolant) are referred to as high-temperature superconductors (HTS). Bednorz and Müller were awarded the Nobel Prize in Physics in 1987 for their work.

Cuprate materials dominate the field of high-temperature superconductors. Their discovery in 1986 led to a flood of activity

and dozens of mixed-metal cuprates were synthesized with ever-increasing T_C 's. These materials are generally characterized as perovskites as they possess a roughly two-metal to three-oxygen ratio. Typical HTS perovskites are mixtures of metals with at least one rare-earth or late p-block metal with a cuprate (copper oxide). Current theory holds that the copper and oxygen atoms will be held in one or more planes in the unit cell. Superconductivity arises from electron interactions in the Cu–O plane. Addition of various other metals to the cuprate is believed to create holes in the Cu–O plane, resulting in new electronic ordered states including a high-temperature superconducting state.

References

- (1) Gvaleri, J. R. *Appl. Phys. Lett.* **1973**, *23*, 480.
- (2) Wu, M. K. et al. *Phys. Rev. Lett.* **1987**, *58*, 908.
- (3) Beno, M. A. et al. *Appl. Phys. Lett.* **1987**, *51*, 57.

Oxides

Name	Formula	MW	CAS	MP	BP	Density at 25 °C	Cat. No.	List Price
Antimony(III) oxide, 99.999%	Sb_2O_3	291.52	[1309-64-4]	655 °C	1550 °C		202649-10G 202649-50G	
Barium oxide, 99.99%	BaO	153.34	[1304-28-5]	1973 °C	2000 °C	5.72 g/mL	554847-5G 554847-25G	
Bismuth(III) oxide, 99.999%	Bi_2O_3	465.96	[1304-76-3]	817 °C	1890 °C	8.0 g/mL	202827-10G 202827-50G 202827-250G	
Calcium oxide, 99.995%	CaO	56.08	[1305-78-8]	2850 °C		3.3 g/mL	229539-5G 229539-50G	
Cerium(IV) oxide, 99.995%	CeO_2	172.12	[1306-38-3]	2400 °C		7.13 g/mL	202975-10G 202975-50G	
Copper(II) oxide, 99.9999%	CuO	79.54	[1317-38-0]	1336 °C		6.31 g/mL	203130-5G 203130-25G 203130-100G	
Europium(III) oxide, 99.999%	Eu_2O_3	351.92	[1308-96-9]	2350 °C		7.42 g/mL	323543-1G 323543-5G	
Gadolinium(III) oxide, 99.99+%	Gd_2O_3	362.50	[12064-62-9]	2330 °C		7.407 g/mL at 20 °C	203297-5G 203297-25G	
Gold(III) oxide hydrate	$Au_2O_3 \cdot xH_2O$	441.93	[1303-58-8]	150 °C (dec.)			334057-500MG 334057-2.5G	
Indium(III) oxide, 99.999%	In_2O_3	277.64	[1312-43-2]	1913 °C		7.18 g/mL	203424-5G 203424-25G	
Lanthanum(III) oxide, 99.999%	La_2O_3	325.82	[1312-81-8]	2305 °C	4200 °C	6.51 g/mL	203556-20G 203556-100G 203556-500G	
Mercury(II) oxide, 99.999%	HgO	216.59	[21908-53-2]	500 °C (dec.)		11.14 g/mL	203793-2G 203793-10G	
Neodymium(III) oxide, 99.99%	Nd_2O_3	336.48	[1313-97-9]	2320 °C		7.24 g/mL at 20 °C	203858-10G 203858-50G	
Strontium oxide, 99.9%	SrO	103.62	[1314-11-0]	2530 °C	3000 °C	4.7 g/mL	415138-10G 415138-50G	
Thallium(III) oxide, 99.99%	Tl_2O_3	456.74	[1314-32-5]	717 °C	875 °C	10.2 g/mL	204617-10G 204617-50G	
Thulium(III) oxide, 99.99%	Tm_2O_3	385.87	[12036-44-1]	2425 °C		8.6 g/mL	204676-1G 204676-5G	
Tin(IV) oxide, 99.995+%	SnO_2	150.69	[18282-10-5]	1630 °C	1900 °C	6.95 g/mL	204714-5G 204714-25G	
Ytterbium(III) oxide, 99.99%	Yb_2O_3	394.08	[1314-37-0]	2435 °C		19.7 g/mL	204889-2G 204889-10G	
Yttrium(III) oxide, 99.999%	Y_2O_3	225.81	[1314-36-9]	2690 °C	4300 °C	5.01 g/mL	204927-2G 204927-10G 204927-50G	

TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit sigma-aldrich.com/matsci.

Carbonates

Barium carbonate, 99.999%

BaCO ₃	
MW: 197.35	
[513-77-9]	
202711-5G	5 g
202711-25G	25 g
202711-100G	100 g
202711-6X100G	6×100 g

Bismuth(III) carbonate basic

(BiO) ₂ CO ₃	
MW: 509.97	
[5892-10-4]	
6.86 g/mL 25 °C	
278947-5G	5 g
278947-100G	100 g
278947-500G	500 g

Calcium carbonate, 99.995+%

CaCO ₃	
MW: 100.09	
[471-34-1]	
2.93 g/mL 25 °C	
202932-5G	5 g
202932-25G	25 g
202932-100G	100 g

Lead(II) carbonate, 99.99+%

PbCO ₃	
MW: 267.2	
[598-63-0]	
335169-25G	25 g

Strontium carbonate, 99.995%

SrCO ₃	
MW: 147.63	
[1633-05-2]	
3.7 g/mL 25 °C	
204455-5G	5 g
204455-25G	25 g
204455-100G	100 g

Thallium(I) carbonate, 99.99+%

Tl ₂ CO ₃	
MW: 468.75	
[6533-73-9]	
MP: 260–270 °C (dec.)	
7.11 g/mL 25°C	
255769-10G	10 g
255769-50G	50 g

Cuprates

Bismuth lead strontium calcium copper oxide, fine powder

Bi _{1.6} Pb _{0.4} Sr _{1.6} Ca _{2.0} Cu _{2.8} O _{9.2+X}	
[116739-98-1]	
378720-10G	10 g
378720-50G	50 g

Bismuth strontium calcium copper oxide, powder, particle size 5 μm

Bi ₂ Sr ₂ CaCu ₂ O _{8+X} , x = 0.15–0.20	
[114901-61-0]	
6.4 g/mL 25 °C	
365106-10G	10 g
365106-50G	50 g

Yttrium barium copper oxide, powder, particle size 2 μm, 99.9%

YBa ₂ Cu ₃ O _x , x ~6.7	
[107539-20-8]	
357464-10G	10 g

Yttrium barium copper oxide carbonate, 99.9%

(Y ₂ O ₃) _{0.5} (BaCO ₃) ₂ (CuO) ₃	
335878-5G	5 g

Nitrates

Barium nitrate, 99.999%

Ba(NO ₃) ₂	
MW: 261.35	
[10022-31-8]	
MP: 592°C (dec.)	
202754-25G	25 g
202754-100G	100 g

Lead(II) nitrate, 99.999%

Pb(NO ₃) ₂	
MW: 333.12	
[10099-74-8]	
MP: 470 °C (dec.)	
203580-10G	10 g
203580-50G	50 g

Strontium nitrate, 99.995%

Sr(NO ₃) ₂	
MW: 211.63	
[10042-76-9]	
MP: 570 °C	
204498-10G	10 g
204498-50G	50 g

Thallium(I) nitrate, 99.999%

TlNO ₃	
MW: 266.38	
[10102-45-1]	
MP: 206 °C	
204609-10G	10 g
204609-25G	25 g
204609-125G	125 g

Piezoelectric Crystals



Dr. Kevin T. Zawilski
BAE Systems, Advanced Systems
and Technology
Merrimack, NH

PMN-PT research performed at Stanford University, Laboratory for Advanced Materials, Stanford, CA

Growth of Lead Magnesium Niobate-Lead Titanate Single Crystals

Piezoelectric materials have the ability to generate a voltage in response to an applied mechanical stress or conversely change shape in response to an applied voltage. High performance piezoelectric materials have a wide range of applications including sonar arrays, ultrasonic imaging devices, and fine motion controllers. A major breakthrough in high performance piezoelectric materials was made in 1997, when the exceptional piezoelectric properties of relaxor ferroelectric single crystals were first measured.^{1,2} When crystals such as lead magnesium niobate-lead titanate, $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - (x)\text{PbTiO}_3$ (or PMN-PT), were measured along the $\langle 001 \rangle$ direction, the electromechanical coupling factor (k_{33}) was found to be $>90\%$ with achievable strain levels of $>1.5\%$. Previously, the best performing piezoelectric materials were $\text{PbZr}_{(1-y)}\text{Ti}_y\text{O}_3$ (PZT) ceramics with k_{33} ranging from 70% to 75% and achievable strain levels of 0.1%.

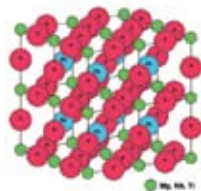


Figure 1. Perovskite structure of PMN-PT

PMN-PT has a perovskite crystal structure as shown in Figure 1 and deforms from the high temperature cubic form to either pseudo-cubic/trigonal form at room temperature and low Ti concentration or tetragonal form at room temperature and high Ti concentration.³ The piezoelectric properties of PMN-PT peak near the morphotropic phase boundary (MPB) where the solid solution changes structure from pseudo-cubic/trigonal to tetragonal, in the range of $x = 0.32-0.35$.

Flux Growth

PMN-PT crystals were first grown by Park and Shrout¹ using the flux technique, and since that time, others have successfully followed their lead.³⁻⁵ The flux growth of this material typically involves dissolving the component oxides in a PbO or $\text{PbO/B}_2\text{O}_3$ flux. When the flux is slowly cooled, PMN-PT crystals begin to spontaneously nucleate and grow. Crystals from one to several mm in cross section have been obtained from such experiments.

Bridgman Growth

The Bridgman method is much more conducive than the flux technique to the growth of the large, oriented crystals required for commercial devices. In the Bridgman method, a PMN-PT charge is

melted in a crucible and then is unidirectionally solidified by passing the crucible through a temperature gradient. An oriented crystal is placed at the cold end of the crucible and partially melted to seed crystal growth. High-temperature furnaces and Pt crucibles are required for the growth of this material because the melting point of PMN-PT is in the range of 1285 °C to 1320 °C.⁶



Figure 2. Typical Bridgman grown PMN-PT crystal (diam. = 1.8 cm)

Several researchers have used this technique to grow large, oriented PMN-PT crystals of good quality.⁶⁻⁹ A typical Bridgman grown crystal with a 1.8-cm diameter is shown in Figure 2. Although single crystals have been grown using this technique, compositional variations along the growth axis are a major problem that results in large portions of the crystals having non-optimal piezoelectric properties.⁶

Zone Leveling

The segregation behavior observed in the Bridgman growth of PMN-PT is a well-recognized consequence of thermodynamic properties of solid-solution systems, in this case the pseudo-binary system of lead magnesium niobate-lead titanate. The zone leveling technique had previously been used to 'level' compositional profiles in other segregating material systems and was proposed as an attractive method to eliminate the compositional variations observed in PMN-PT. Instead of melting the entire charge, as in Bridgman growth, the zone leveling method relies on melting only a small 'zone' of charge. By placing the initial molten zone partway into a seed and subsequently passing the zone through the entire charge, large, oriented single crystals of relatively good compositional uniformity can be grown.¹⁰

Some potentially difficult challenges remain in the production of PMN-PT for commercial devices. These include scaling laboratory processes to reproducible production scales and determining how to lower production costs (for example the expensive Pt crucibles can only be used once in the growth processes described previously). The physics and chemistry of PMN-PT are still being fully explored, making this new material very exciting and possibly opening doors to more applications.

References

- (1) Park, S.-E.; Shrout, T. R. *J. Appl. Phys.* **1997**, *82*, 1804.
- (2) Service, R. F. *Science* **1997**, *275*, 1878.
- (3) Ye, Z.-G.; Dong, M. *J. Appl. Phys.* **2000**, *87*, 2312.
- (4) Dong, M.; Ye, Z.-G. *J. Cryst. Growth* **2000**, *209*, 81.
- (5) Jiang, X. et al. *Physica C* **2001**, *364-365*, 678.
- (6) Zawilski, K. T. et al. *J. Cryst. Growth* **2003**, *258*, 353.
- (7) Lee, S.-G. et al. *Appl. Phys. Lett.* **1999**, *74*, 1030.
- (8) Zawilski, K. T. et al. *J. Cryst. Growth* **2005**, *282*, 236.
- (9) X. Wan, X. et al. *J. Cryst. Growth* **2004**, *263*, 251.
- (10) Zawilski, K. T. et al. *J. Cryst. Growth* **2005**, *277*, 393.

Name	Formula	MW	CAS	MP	BP	Density at 25 °C	Cat. No.	List Price
Boric anhydride, 99.999%	B_2O_3	69.62	[1303-86-2]	450 °C	2065 °C	2.46 g/mL	202851-5G 202851-25G	
Lead(II) oxide, 99.999%	PbO	223.19	[1317-36-8]	886 °C		9.35 g/mL	203610-10G 203610-50G	
Lead(II) titanate, 99+%	PbTiO_3	303.09	[12060-00-3]			7.52 g/mL	215805-250G	
Magnesium oxide, 99.999%	MgO	40.31	[1309-48-4]	2852 °C	3600 °C	3.60 g/mL	529699-10G 529699-50G	
Niobium(V) oxide, 99.99%	Nb_2O_5	265.81	[1313-96-8]	1460 °C		4.47 g/mL	203920-10G 203920-50G	
Titanium(IV) oxide, rutile, 99.999%	TiO_2	79.87	[1317-80-2]	1800 °C		4.17 g/mL	204730-5G 204730-25G	

TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit sigma-aldrich.com/matsci.

Solid-State Metathesis Materials Synthesis



Dr. Richard G. Blair
Materials and Device Technologies Division,
Jet Propulsion Laboratory Pasadena, CA

Prof. Richard B. Kaner
Department of Chemistry & Biochemistry
and California NanoSystems Institute,
University of California, Los Angeles, CA

In the last two decades, a new method termed solid-state metathesis (SSM) has been developed to synthesize compounds that are often difficult to produce conventionally. Alkali or alkaline-earth metal main group compounds are combined with halides to form oxides,¹⁻⁷ sulfides,^{3,8} selenides,^{3,8} tellurides,³ nitrides,⁹⁻¹⁵ phosphides,¹⁶⁻¹⁸ arsenides,¹⁷ antimonides,¹⁷ carbides,^{19,20} silicides,²¹ borides,^{15,22,23} and aluminides.²⁴ Additionally, nanostructured materials such as nanotubes,²⁵ nanocrystals,^{26,27} and high-surface-area materials²⁸ can be produced. These reactions provide a novel tool for preparing difficult-to-synthesize materials. Although the precursor is usually a halide, an oxide can be used as well. For example, we have shown that MgSiN₂ can be synthesized by reacting SiO₂ with Mg₃N₂.¹³ Oxides have also been successfully used as precursors for hydroxyapatite²⁹ and silicides.²¹

The driving force behind solid-state metathesis reactions is the formation of stable byproducts. For example, combining Ga₃ with Li₃N to produce GaN, as given in **Scheme 1**, has a ΔH_{rxn} of -515 kJ.



Scheme 1. Solid-state metathesis of gallium nitride

This is more than four times as energetic as the elemental reaction $\text{Ga} + 0.5\text{N}_2 \rightarrow \text{GaN}$ (ΔH = -110 kJ).

SSM reactions can be initiated by flame, furnace, heated filament, ball mill, or microwave. The phase produced is often determined by the rate of the reaction.²⁴ Similarly, the reaction rate can be tuned to control the crystallite size of the products formed.⁹ Diluents or fast reaction times can be used to produce nanoscale powders or materials with high surface areas.⁹

In a typical SSM reaction, an alkali or alkaline-earth metal compound with the desired anion is reacted with a metal halide or oxide. Reaction temperatures are controlled through the choice of halide, alkali or alkaline-earth metal,³⁰ dilution, and vessel design. It is important to note that the driving force for these reactions is the heat released by the formation of alkali or alkaline-earth halides.

Alkali halides usually have lower heats of formation than alkaline-earth halides, so reactions utilizing alkaline-earth metals will generally result in higher reaction temperatures. The upper limit of the reaction temperature is usually governed by the boiling point of the salt produced. Alkaline-earth salts have higher melting and boiling points, thereby increasing the upper limit of the reaction temperature.

The heavier the halogen used, generally the lower the reaction temperature. This can be useful for the synthesis of compounds that are unstable at high temperatures. For example, it is easier to obtain GaN from GaI₃ than GaCl₃ in a reaction with Li₃N,¹⁰ due to the differences in heats of formation of LiI (ΔH = -270.4 kJ/mol) vs LiCl (ΔH = -408.5). Conversely, the synthesis of some materials is favored by high temperatures. The use of AlCl₃ is a better choice than AlI₃ when preparing AlN from the reaction with Ca₃N₂.⁹

Another effective method for lowering a reaction temperature is by using a diluent.³¹ This can be realized by adding inert salts, such as the byproduct salt itself, to the reaction mixture. This process can be improved for nitrides by adding low-melting or -vaporizing nitrogen containing compounds (like NH₂Cl or LiNH₂).¹⁰ Not only do these compounds act as a heat sink, but they can supply nitrogen to the reaction as well.

A final method for reducing a reaction temperature is by controlling the heat loss. In this way, these reactions can be effectively scaled up without producing destructive amounts of heat. This can be achieved by specifically designing the reaction vessel¹⁰ or by controlling the amount of heat produced by slow addition of precursors into the reactor. If a hotter reaction is desired, choose the starting materials carefully or begin these reactions at an elevated temperature.

In summary, solid-state metathesis (SSM) reactions have developed over the past two decades into an effective method for synthesizing materials that are difficult to make by conventional methods.³¹

References

- Gillan, E. G.; Kaner, R. B. *J. Mater. Chem.* **2001**, *11*, 1951.
- Wiley, J. B. et al. *Mater. Res. Bull.* **1993**, *28*, 893.
- Parkin, I. P.; Rowley, A. T. *Polyhedron* **1993**, *12*, 2961.
- Hector, A.; Parkin, I. P. *Polyhedron* **1993**, *12*, 1855.
- Hector, A.; Parkin, I. P. *J. Mater. Sci. Lett.* **1994**, *13*, 219.
- Mandal, T. K.; Gopalakrishnan, J. *J. Mater. Chem.* **2004**, *14*, 1273.
- Parhi, P. et al. *Mater. Lett.* **2004**, *58*, 3610.
- Bonneau, P. R. et al. *Inorg. Chem.* **1992**, *31*, 2127.
- Janes, R. A. et al. *Inorg. Chem.* **2003**, *42*, 2714.
- Cumberland, R. W. et al. *J. Phys. Chem. B* **2001**, *105*, 11922.
- O'Loughlin, J. L. et al. *Inorg. Chem.* **2001**, *40*, 2240.
- Wallace, C. H. et al. *Appl. Phys. Lett.* **1998**, *72*, 596.
- Blair, R. G. et al. *Chem. Mater.* **2005**, *17*, 2155.
- Shemkunas, M. P. et al. *J. Am. Cer. Soc.* **2002**, *85*, 101.
- Gibson, K. et al. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1863.
- Jarvis, R. F., Jr. et al. *Inorg. Chem.* **2000**, *39*, 3243.
- Treece, R. E. et al. *Inorg. Chem.* **1994**, *33*, 5701.
- Rowley, A. T.; Parkin, I. P. *J. Mater. Chem.* **1993**, *3*, 689.
- Nartowski, A. M. et al. *J. Mater. Chem.* **1999**, *9*, 1275.
- Nartowski, A. M. et al. *J. Mater. Chem.* **2001**, *11*, 3116.
- Nartowski, A. M.; Parkin, I. P. *Polyhedron* **2002**, *21*, 187.
- Rao, L. et al. *J. Mater. Res.* **1995**, *10*, 353.
- Lupinetti, A. J. et al. *Inorg. Chem.* **2002**, *41*, 2316.
- Blair, R. G. et al. *Chem. Mater.* **2003**, *15*, 3286.
- O'Loughlin, J. L. et al. *J. Phys. Chem. B* **2001**, *105*, 1921.
- Ye, X. R. et al. *Adv. Mater.* **1999**, *11*, 941.
- McMillan, P. F. et al. *J. Solid State Chem.* **2005**, *178*, 937.
- Janes, R. A. et al. *Chem. Mater.* **2003**, *15*, 4431.
- Feng, J. et al. *Wuji Huaxue Xuebao* **2005**, *21*, 801.
- Parkin, I. P.; Nartowski, A. M. *Polyhedron* **1998**, *17*, 2617.
- Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996**, *8*, 333.

For questions, product data, or new product suggestions,
please contact the Materials Science Team: matsci@sial.com.

Alkali and Alkaline-Earth Salts

Ammonium chloride, 99.998%

NH ₄ Cl	
MW: 53.49	
[12125-02-9]	
MP: 340 °C (subl.)	
254134-5G	5 g
254134-25G	25 g
254134-100G	100 g

Calcium nitride, particle size –200 mesh, 95%

Ca ₃ N ₂	
MW: 148.25	
[12013-82-0]	
MP: 1195 °C	
2.63 g/mL 25 °C	
415103-25G	25 g
415103-100G	100 g

Lithium amide, powder, 95%

LiNH ₂	
MW: 22.96	
[7782-89-0]	
1.178 g/mL 25 °C	
213217-5G	5 g
213217-100G	100 g
213217-500G	500 g

Lithium nitride, particle size –80 mesh

Li ₃ N	
MW: 34.82	
[26134-62-3]	
MP: 813 °C	
1.3 g/mL 25 °C	
399558-5G	5 g
399558-25G	25 g

Magnesium silicide, 99+%, particle size –20 mesh

Mg ₂ Si	
MW: 76.71	
[22831-39-6]	
343196-25G	25 g

Sodium azide, 99.99+%

NaN ₃	
MW: 65.01	
[26628-22-8]	
438456-5G	5 g
438456-25G	25 g

Sodium peroxide, reagent grade, 97%, granular, particle size 140 mesh

Na ₂ O ₂	
MW: 77.98	
[1313-60-6]	
MP: 460 °C (dec.)	
2.805 g/mL 25 °C	
223417-5G	5 g
223417-100G	100 g
223417-500G	500 g

Sodium sulfide

Na ₂ S	
MW: 78.04	
[1313-82-2]	
MP: 950 °C	
1.86 g/mL 25 °C	
407410-10G	10 g
407410-50G	50 g

Halides

Name	Formula	MW	CAS	MP	BP	Density at 25 °C	Cat. No.	List Price
Aluminum chloride, 99.99%	AlCl ₃	133.34	[7446-70-0]	190 °C		2.48 g/mL	449598-5G 449598-25G	
Copper(II) fluoride, hydrate, 99.999%	CuF ₂ · xH ₂ O	101.54		785 °C	1676 °C	2.93 g/mL	401536-5G 401536-25G	
Gallium(III) chloride, beads, –10 mesh, 99.999+%	GaCl ₃	176.08	[13450-90-3]	78 °C	201 °C	2.47 g/mL	427128-5G 427128-25G 427128-100G	
Gallium(III) iodide, 99.999%	GaI ₃	450.43	[13450-91-4]	345 °C (subl.)		4.15 g/mL	429341-1G 429341-5G	
Hafnium(IV) chloride, 98%	HfCl ₄	320.3	[13499-05-3]	432 °C			258202-10G 258202-50G	
Molybdenum(V) chloride, 95%	MoCl ₅	273.21	[10241-05-1]	194 °C	268 °C	2.928 g/mL	208353-25G 208353-100G	
Niobium(V) chloride, 99.999%	NbCl ₅	270.17	[10026-12-7]	204.7 °C	254 °C	2.75 g/mL	510696-5G 510696-25G	
Ammonium chloride, 99.998%	NH ₄ Cl	53.49	[12125-02-9]	340 °C (subl.)			254134-5G 254134-25G 254134-100G	
Tantalum(V) chloride, 99.999%	TaCl ₅	358.21	[7721-01-9]	210 °C	233 °C	3.68 g/mL	510688-5G 510688-25G	
Tungsten(VI) chloride, 99.9+%	WCl ₆	396.57	[13283-01-7]	275 °C	347 °C	3.52 g/mL	241911-10G 241911-100G	
Zirconium(IV) chloride, 99.9+%	ZrCl ₄	233.03	[10026-11-6]		331 °C	2.8 g/mL	357405-10G 357405-100G	

TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit sigma-aldrich.com/matsci.

Solvothermal Synthesis of Nanoparticles



Prof. Bonnie Gersten
Queens College of the City University
of New York

Solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. The process involves the use of a solvent under moderate to high pressure (typically between 1 atm and 10,000 atm)

and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction of precursors during synthesis. If water is used as the solvent, the method is called “hydrothermal synthesis.” The synthesis under hydrothermal conditions is usually performed below the supercritical temperature of water (374 °C). The process can be used to prepare many geometries including thin films, bulk powders, single crystals, and nanocrystals. In addition, the morphology (sphere (3D), rod (2D), or wire (1D)) of the crystals formed is controlled by manipulating the solvent supersaturation, chemical of interest concentration, and kinetic control. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic routes. Over the last decade, a majority (~80%) of the literature concerning solvothermal synthesis has focused on nanocrystals; therefore, this review will highlight some advances in nanocrystalline, solvothermal synthesis.

Interest in nanocrystals is driven by their unique properties. One example of the unique properties of nanocrystals is illustrated by the discovery of solvothermally synthesized quantum dots (QDs). Luis Brus^{1,2} first explained that hydrothermally prepared nanoparticles of cadmium sulfide, CdS, in an aqueous suspension, had a blue shift in the visible absorption and emission spectra compared with bulk CdS. Particles whose radius is less than the Exciton Bohr Radius exhibit discrete energy levels similar to single atoms. Unlike the band energies observed in bulk materials, every unique crystal diameter on the nanoscale corresponds to a discrete energy. Materials that exhibit this characteristic are called “artificial atoms” or quantum dots. Recent reviews³⁻⁵ elucidate the degree to which solvothermal synthetic techniques are now an essential technique for controlling the size of the II–VI and III–V semiconductor materials. Synthesis of the QDs typically requires a cation source material that is soluble in the chosen solvent and a surfactant that caps or stabilizes the quantum dot, arresting its growth. For example, CdSe QDs are prepared by dissolving CdO in trioctylphosphine oxide (TOPO) and trioctyl phosphine (TOP), which acts as both a solvent and capping agent. The solution is heated to 300 °C, after which elemental selenium dissolved in tributylphosphine (TBP) is added. The reaction is then quenched and nanocrystals are observed.⁶

Zinc oxide is another example of a II–VI compound that can be prepared solvothermally and will exhibit quantum dot effects.⁷ In one method, zinc acetate dihydrate was dissolved in 2-propanol at 50 °C. Subsequently, the solution was cooled to 0 °C and NaOH was added to precipitate ZnO. The solution was then heated to 65 °C to allow ZnO growth for a period of time before a capping agent (1-dodecanethiol) was injected into the suspension to arrest the growth. The rod-shaped ZnO nanocrystals (**Figure 1**) exhibit an absorption spectrum (**Figure 2**) indicative of the quantum effect.

Quantum dots can be synthesized by the solvothermal route in many shapes including spheres, rods, tetrapods, and teardrops by controlling the temperature, concentration, and reaction time.⁸ Additionally, a shell of one composition (e.g., ZnS) can be synthesized over a core of another nanocrystal (e.g., CdS).⁹ The core can also be used as a seed to grow larger particles by adjusting the concentration after the initial growth. Many quantum dot applications are optimized by size and shape control, and solvothermal synthesis is a key technology for achieving this control.

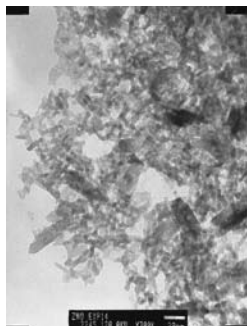


Figure 1. TEM micrograph of ZnO rods

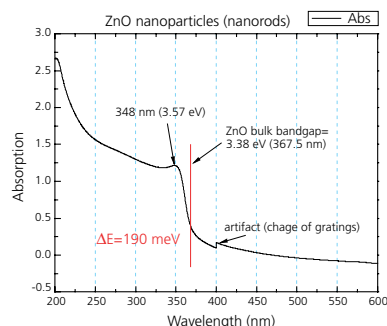


Figure 2. Absorption plot of ZnO rods showing quantum dot effect

Compared to II–VI materials, III–V compounds are more difficult to process by the solvothermal method.⁴ One method of synthesis of nanosized InSb is the reduction of InCl_3 and SbCl_3 , by NaBH_4 at 200 °C, using diethylenediamine (DETA) as a solvent.¹⁰ This material was irregularly shaped and agglomerated and therefore did not exhibit the quantum dot effect. However, recent work on phosphide (InP) and nitride (GaN), as well as arsenide (GaAs) III–V semiconductors, did exhibit quantum dot properties.

Although metallic particles can also exhibit the quantum dot behavior, their Exciton Bohr Radius is much smaller than the semiconductors, resulting in significant synthetic challenges. However, metallic nanoparticle synthesis is of current interest for applications in nanocircuits and devices. The size, shape, and type of material desired depends on the application. For example, the desire for higher density magnetic recording devices initiated the development of a new nano-sized ferromagnetic material based on the 3D self-assembly of two distinct sizes of magnetic particles of Fe_3O_4 (8 nm) and $\text{Fe}_{58}\text{Pt}_{42}$ (4 nm) into a superlattice colloidal crystal.¹¹ The self-assembly occurs when the particles have less than a 5% size distribution. The monosized Fe_3O_4 particles were prepared from iron (III) acetylacetonate, in phenyl ether in the presence of alcohol, oleic acid, and oleylamine at 265 °C.¹¹ The monosized $\text{Fe}_{58}\text{Pt}_{42}$ was synthesized by the reduction of platinum acetylacetonate by 1,2-hexadecanediol and the decomposition of iron pentacarbonyl in the presence of oleic acid and oleyl amine stabilizers.¹¹

Similar types of magnetic particles, as well as metallic nanoparticles and quantum dots, are finding applications in biosensors. These nanoparticles require hydrophilic surface moieties in order to be compatible with biomolecules. Hydrothermally prepared nanoparticles are particularly suited to biotech applications because the nanoparticles are hydrophilic due to surface hydroxyl groups. However, these hydroxyls often influence the properties of interest in the nanoparticle (e.g., reduce the quantum yield of QDs or oxidize the surface of metals). Other solvothermal routes, however, can be used to prepare nanoparticles which, upon the addition of surfactants, are made hydrophilic. Gold particles are of particular interest because of their inert nature. Monosized gold particles were prepared by the solvothermal reduction process similar to that described by Chen and Kimura.¹² In this method, hydrogen tetrachloroaurate tetrahydrate was reduced with sodium borohydride and mercaptosuccinic acid was used as a stabilizer. **Figure 3** displays a micrograph of gold nanoparticles self-assembled onto a copper surface.

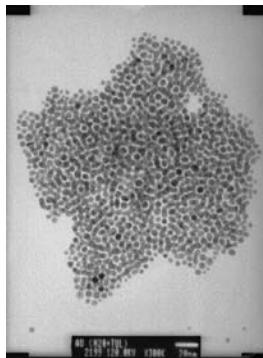


Figure 3. TEM micrograph of self-assembled gold particles

For questions, product data, or new product suggestions,
please contact the Materials Science Team: matsci@sial.com.

In summary, the solvothermal synthesis of nanoparticles is finding wide applications from nanocircuits and nano-optical circuits to nanomagnetism and biotech. The ability to control the size and shape of a host of materials makes this technique versatile, economical, and facile.

References

- (1) Rossetti, R.; Brus, L. *J. Phys. Chem.* **1982**, *86*, 4470.
- (2) Brus, L. *J. Chem Phys.* **1984**, *80*, 4403.
- (3) Esteves, A.C.C.; Trindade, T. *Curr. Opin. Solid State Mater. Chem.* **2002**, *6*, 347.
- (4) Green, M. *ibid.* **2002**, *6*, 355.
- (5) Rajamathia, M.; Seshadri, R. *ibid.* **2002**, *6*, 337.
- (6) Peng, Q. et al. *Inorg. Chem.* **2001**, *40*, 3840.
- (7) Wong, E. M. et al. *Langmuir* **2001**, *17*, 8362.
- (8) Manna, L. et al. *J. Am. Chem. Soc.* **2000**, *122*, 12702.
- (9) Manna, L. et al. *J. Am. Chem. Soc.* **2002**, *124*, 7136.
- (10) Gersten, B. et al. *Mater. Res. Soc. Symp. Proc.* **2005**, *848*, FF3.34.1.
- (11) Zeng, H. et al. *Nature* **2002**, *420*, 395.
- (12) Chen, S.; Kimura, K. *Langmuir* **1999**, *15*, 1075.

Reagents

Antimony(III) chloride, 99.99+%

SbCl ₃	
MW: 228.12	
[10025-91-9]	
MP: 73.4 °C	
BP: 223 °C	
3.14 g/mL at 25 °C	
337374-10G	10 g
337374-100G	100 g

Arsenic(III) chloride, 99.99%

AsCl ₃	
MW: 181.28	
[7784-34-1]	
MP: -16 °C	
BP: 130.2 °C	
2.15 g/mL at 25 °C	
200077-25G	25 g
200077-50G	50 g

Cadmium oxide, 99.99+%

CdO	
MW: 128.41	
[1306-19-0]	
MP: ~1500 °C	
BP: 1559 °C	
8.15 g/mL at 25 °C	
202894-5G	5 g
202894-25G	25 g

Gallium(III) chloride, anhydrous, beads, -10 mesh, 99.99%

GaCl ₃	
MW: 176.08	
[13450-90-3]	
MP: 78 °C	
BP: 201 °C	
2.47 g/mL at 25 °C	
450898-5G	5 g
450898-25G	25 g
450898-50G	50 g

Gallium(III) chloride, anhydrous, beads, -10 mesh, 99.999+%

GaCl ₃	
MW: 176.08	
[13450-90-3]	
MP: 78 °C	
BP: 201 °C	
2.47 g/mL at 25 °C	
427128-5G	5 g
427128-25G	25 g
427128-100G	100 g
427128-6X100G	6x100 g

Hydrogen tetrachloroaurate(III) trihydrate, 99.9+%, Engelhard code S3300

HAuCl ₄ · 3H ₂ O	
MW: 393.83	
[16961-25-4]	
520918-1G	1 g
520918-5G	5 g
520918-25G	25 g

Indium(III) acetylacetonate, 99.99+%

In(C ₅ H ₇ O ₂) ₃	
MW: 412.15	
[14405-45-9]	
MP: 187-189 °C	
I3300-1G	1 g
I3300-5G	5 g

Indium(III) chloride, 99.999%

InCl ₃	
MW: 221.18	
[10025-82-8]	
MP: 583 °C	
3.46 g/mL at 25 °C	
203440-1G	1 g
203440-10G	10 g
203440-50G	50 g

Iron(0) pentacarbonyl, 99.999%

Fe(CO) ₅	
MW: 195.9	
[13463-40-6]	
MP: -20 °C	
BP: 103 °C	
1.49 g/mL at 25 °C	
481718-25ML	25 mL
481718-100ML	100 mL

Iron(III) acetylacetonate, 99.9+%

Fe(C ₅ H ₇ O ₂) ₃	
MW: 353.18	
[14024-18-1]	
MP: 180-182 °C (dec.)	
5.24 g/mL at 25 °C	
517003-10G	10 g
517003-50G	50 g

Platinum(II) acetylacetonate, 99.99%

Pt(C ₅ H ₇ O ₂) ₂	
MW: 393.31	
[15170-57-7]	
MP: 249-252 °C	
523038-1G	1 g

Selenium, powder, -100 mesh, 99.99%

Se
MW: 78.96
[7782-49-2]
MP: 217 °C
BP: 684.9 °C
4.81 g/mL at 25 °C

229865-5G	5 g
229865-20G	20 g
229865-100G	100 g

Sodium borohydride, 99%

NaBH₄
MW: 37.83
[16940-66-2]
MP: >300 °C (dec.)

213462-25G	25 g
213462-100G	100 g

Sulfur, 99.998%

S
MW: 37.8
[7704-34-9]
MP: 117–120 °C
BP: 444.7 °C
2.07 g/mL at 25 °C

213292-10G	10 g
213292-50G	50 g
213292-250G	250 g

Zinc acetate dihydrate, 99.999%

Zn(CH₃COO)₂ · 2H₂O
MW: 219.5
[5970-45-6]

379786-5G	5 g
379786-25G	25 g

Solvents**1-Dodecanethiol, 98+%**

CH₃(CH₂)₁₁SH
MW: 202.4
[112-55-0]
BP: 266–283 °C
0.845 g/mL at 25 °C

471364-100ML	100 mL
471364-500ML	500 mL
471364-2L	2 L
471364-18L	18 L

Mercaptosuccinic acid, 97%

HOOCCH(SH)CH₂COOH
MW: 150.15
[70-49-5]
MP: 155–157 °C

M6182-5G	5 g
M6182-25G	25 g
M6182-100G	100 g
M6182-500G	500 g

Octadecylamine, 97%

CH₃(CH₂)₁₇NH₂
MW: 269.52
[124-30-1]
MP: 50–52 °C
BP: 232 °C (32 mm Hg)

305391-25G	25 g
305391-100G	100 g

Oleylamine, tech., 70%

CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂
MW: 267.5
[112-90-3]
BP: 348–350 °C
0.813 g/mL at 25 °C

O7805-5G	5 g
O7805-100G	100 g
O7805-500G	500 g

Tributylphosphine, 97%

[CH₃(CH₂)₃]₃P
MW: 202.32
[998-40-3]
BP: 150 °C (50 mm Hg)
0.81 g/mL at 25 °C

T49484-5ML	5 mL
T49484-25ML	25 mL

Tributylphosphine, 97%

[CH₃(CH₂)₃]₃P
MW: 202.32
[998-40-3]
BP: 150 °C (50 mm Hg)
0.81 g/mL at 25 °C

247049-100G	100 g
247049-500G	500 g

Trioctylphosphine oxide, ReagentPlus®, 99%

[CH₃(CH₂)₇]₃OP
MW: 386.65
[78-50-2]
MP: 50–52 °C
BP: 201–202 °C (2mm Hg)

223301-5G	5 g
223301-25G	25 g
223301-100G	100 g

Trioctylphosphine, tech., 90%

[CH₃(CH₂)₇]₃P
MW: 370.65
[4731-53-7]
BP: 284–291 °C (50mm Hg)
0.831 g/mL at 25 °C

117854-25ML	25 mL
117854-100ML	100 mL
117854-500ML	500 mL

Tris(trimethylsilyl)phosphine, 95%

[(CH₃)₃Si]₃P
MW: 250.55
[15573-38-3]
BP: 243–244 °C
0.863 g/mL at 25 °C

333670-1G	1 g
-----------	-----

Intermetallic Compounds of Antimony and Bismuth



Prof. Arthur Mar
Department of Chemistry
University of Alberta, Edmonton, AB
Canada

Intermetallic compounds consist of combinations of metals in definite stoichiometric proportions. Given the predominance of metallic elements in the periodic table, the number of

combinations is enormous. In the last decade, we have investigated the intermetallic chemistry of antimony, and more recently, bismuth. Various antimonides have elicited interest for their physical properties, such as $\text{LaFe}_3\text{CoSb}_{12}$ (thermoelectric), $\text{Eu}_{14}\text{MnSb}_{11}$ (colossal magnetoresistance), and $\text{Ce}_3\text{Pt}_3\text{Sb}_4$ (heavy fermions). Our interest has focused on structural relationships, bonding, and properties.

Rare-Earth Compounds

Ternary systems RE-M-Pn consisting of a rare-earth element (RE), a d-block or p-block metal (M), and Sb or Bi (Pn = pnictogen) provide several fascinating examples of compounds where extensive pnictogen–pnictogen bonding occurs in their crystal structures.¹ In $\text{La}_{13}\text{Ga}_8\text{Sb}_{21}$ (Figure 1), five-atom-wide ribbons of Sb atoms that are linked by nearly planar Ga_6 rings define channels in which assemblies of La_6 trigonal prisms reside. Interestingly, $\text{La}_{13}\text{Ga}_8\text{Sb}_{21}$ undergoes a superconducting transition below 2.5 K.²

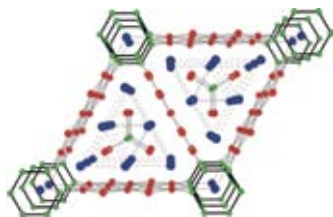


Figure 1. Crystal structure of $\text{La}_{13}\text{Ga}_8\text{Sb}_{21}$

Related compounds are $\text{RE}_6\text{Ge}_{5-x}\text{Sb}_{11+x}$, which contains three- and four-atom-wide Sb ribbons,³ and LaGaBi_2 , which contains three-atom-wide Bi ribbons.⁴ When M is a d-block metal, magnetic ordering frequently develops through the coupling of f electrons of the rare-earth atoms via the d electrons of the transition-metal atoms. For example, ferromagnetic ordering is observed in the series of RECrSb_3 compounds.^{5,6} Syntheses of these compounds generally proceed by direct reaction of the elemental components, either by arc-melting or in furnaces at high temperatures (up to 1000 °C).

Antimony, powder, particle size –100 mesh, 99.995%

Sb
MW: 121.75
[7440-36-0]
MP: 630 °C
BP: 1950 °C
6.69 g/mL at 25 °C

264849-25G	25 g
264849-100G	100 g

Bismuth, powder, particle size –100 mesh, 99.999+%

Bi
MW: 208.98
[7440-69-9]
MP: 271 °C
BP: 1560 °C
9.8 g/mL at 25 °C

202819-20G	20 g
202819-100G	100 g

Transition-Metal Compounds

Although many binary intermetallic systems have been thoroughly investigated, surprises remain to be found. The Zr–Sb binary system is very rich, containing the compounds Zr_3Sb , Zr_2Sb , Zr_5Sb_3 , $\text{Zr}_{11}\text{Sb}_{18}$, and ZrSb_2 .⁷ Recently we discovered a new phase of composition Zr_7Sb_4 by arc-melting of the elements followed by annealing.⁸ It exists only within a narrow temperature range (1000–1150 °C). The structure

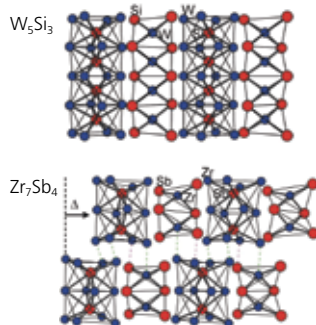


Figure 2. Crystal structure of W_5Si_3 and Zr_7Sb_4

of Zr_7Sb_4 follows an elegant relationship with the W_5Si_3 -type structure (Figure 2). The two-slab-thick slices of Zr_7Sb_4 are held together by strong Zr–Zr and Zr–Sb interlayer bonding interactions. The W_5Si_3 -type structure is an important and common one for intermetallic compounds that is also adopted by ternary transition-metal antimonides and bismuthides such as $\text{Zr}_5\text{M}_{1-x}\text{Pn}_{2+x}$ (M = Cr, Mn; Pn = Sb, Bi).⁹ With four different atomic sites, the W_5Si_3 -type

structure allows many possibilities for substitutional variation, so that even-ordered structures can be obtained with quaternary compounds such as $\text{Nb}_4\text{Pd}_{0.5}\text{SiSb}$.^{2,10}

References

- Mar, A. et al. *Coord. Chem. Rev.* **2002**, 233–234c, 207.
- Mar, A. et al. *Chem. Mater.* **2001**, 13, 1778.
- Mar, A. et al. *Inorg. Chem.* **2001**, 40, 952.
- Mar, A. et al. *Inorg. Chem.* **2003**, 42, 1549.
- Mar, A. et al. *Chem. Mater.* **1998**, 10, 3630.
- Deakin, L. et al. *Chem. Mater.* **2001**, 13, 1778.
- Garcia, E.; Corbett, J. D. *J. Solid State Chem.* **1988**, 73, 440.
- Tkachuk, A. V.; Mar, A. *Inorg. Chem.* **2004**, 43, 4400.
- Tkachuk, A. V.; Mar, A. *J. Solid State Chem.* **2004**, 177, 4136.
- Mar, A. et al. *Inorg. Chem.* **2001**, 40, 5199.

Gallium, 99.9999%

Ga
MW: 69.72
[7440-55-3]
MP: 29.8 °C
BP: 2403 °C
5.904 g/mL at 25 °C

203319-1G	1 g
203319-5G	5 g
203319-25G	25 g

Germanium, powder, particle size –100 mesh, 9.999+%

Ge
MW: 72.59
[7440-56-4]
MP: 937 °C
BP: 2830 °C
5.35 g/mL at 25 °C

327395-5G	5 g
327395-25G	25 g



Thermolyne® 21100 Tube Furnace

Recommended for use with flash-vacuum thermolysis apparatus. Features accurate, automatic temperature control with self-tuning function that maintains preset temperature. LCD display shows both set point and chamber temperature (100 to 1,200 °C). Heating elements embedded in ceramic fiber insulation for rapid heatup and cool down. Adjustable alarm or OTP temperature setting can be used to protect the furnace or loads in the chamber from excess heat. Chamber supplied with two interchangeable end pieces to accept 2.5- and 5.0-cm tube diameters. Furnace operates in any position. Includes line cord and plug.

Cat. No.	AC input	Price
Z229725-1EA	120 V	
Z229733-1EA	240 V	

Solid-State Chemistry Books from



Synthesis of Inorganic Materials

U. Schubert and N. Hüsing, John Wiley & Sons, 2000, 414pp. Softcover.

The preparation process of inorganic materials is one of the most important aspects of material science. The proper choice of the chemical precursors and the preparation technique to obtain a material with the desired chemical and physical properties is a challenge for both material scientists and inorganic chemists. This is the first book to give a comprehensive overview of the current methods for chemical synthesis of inorganic materials. The spectrum ranges from solid-state reactions, CVD, reactions of aqueous systems, preparation and modification of inorganic polymers to the synthesis of tailored porous materials. With examples of selected technically applied materials for each method, the general principles, the material properties, and application of the resulting products are discussed. Numerous tables with further examples help to assess the scope and limitation of the various method. Directed to students in chemistry, material sciences, and physics, this book will also be appreciated by advanced scientists in these fields.

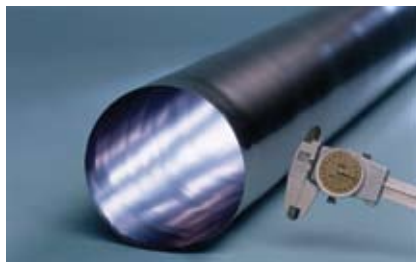
Z511765-1EA

Reactions and Characterization of Solids

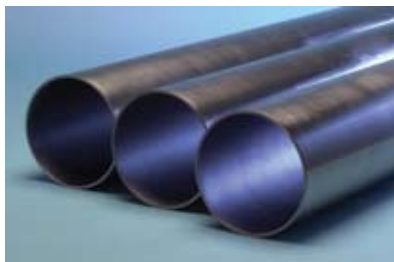
S. Dann, John Wiley & Sons, 2002, 201pp. Softcover.

Solid-state chemistry, in particular the scientific significance of understanding the relationship between chemical structure and physical properties, now forms an important part of both mainstream chemistry and material science degrees. This book is an introductory text with plenty of illustrative examples to reinforce the essentials of the topic. Elementary crystal chemistry and thermodynamics are included to introduce the idea of bond strength as a method of determining and predicting compound stability. General physical properties such as electronic and magnetic behaviour are discussed, together with specific topics relating to solid-state materials such as non-stoichiometry. Several solid-state materials are described in detail, relating the fundamental properties and structural behaviour to real systems and working materials.

Z514802-1EA



Niobium tubing



Tantalum tubing

Description	length × diam. (mm)	MP	BP	Cat. No.	Price
Niobium tubing	500 × 10	2477 °C	4744 °C	Z657727-1EA Z657727-20X1EA	
Tantalum tubing	500 × 10	3017 °C	5458 °C	Z657719-1EA Z657719-20X1EA	

For questions, product data, or new product suggestions,
please contact the Materials Science Team: matsci@sial.com.

Argentina

SIGMA-ALDRICH DE ARGENTINA, S.A.
Tel: 54 11 4556 1472
Fax: 54 11 4552 1698

Australia

SIGMA-ALDRICH PTY., LIMITED
Free Tel: 1800 800 097
Free Fax: 1800 800 096
Tel: 612 9841 0555
Fax: 612 9841 0500

Austria

SIGMA-ALDRICH HANDELS GmbH
Tel: 43 1 605 81 10
Fax: 43 1 605 81 20

Belgium

SIGMA-ALDRICH NV/SA.
Free Tel: 0800-14747
Free Fax: 0800-14745
Tel: 03 899 13 01
Fax: 03 899 13 11

Brazil

SIGMA-ALDRICH BRASIL LTDA.
Tel: 55 11 3732-3100
Fax: 55 11 3733-5151

Canada

SIGMA-ALDRICH CANADA LTD.
Free Tel: 800-565-1400
Free Fax: 800-265-3858
Tel: 905-829-9500
Fax: 905-829-9292

China

SIGMA-ALDRICH CHINA INC.
Tel: 86-21-6386 2766
Fax: 86-21-6386 3966

Czech Republic

SIGMA-ALDRICH S.R.O.
Tel: +420 246 003 200
Fax: +420 246 003 291

Denmark

SIGMA-ALDRICH DENMARK A/S
Tel: 43 56 59 10
Fax: 43 56 59 05

Finland

SIGMA-ALDRICH FINLAND
Tel: (09) 350 9250
Fax: (09) 350 9255

France

SIGMA-ALDRICH CHIMIE S.à.r.l.
Tel appel gratuit: 0800 211 408
Fax appel gratuit: 0800 031 052

Germany

SIGMA-ALDRICH CHEMIE GmbH
Free Tel: 0800-51 55 000
Free Fax: 0800-649 00 00

Greece

SIGMA-ALDRICH (O.M.) LTD
Tel: 30 210 9948010
Fax: 30 210 9943831

Hungary

SIGMA-ALDRICH Kft
Tel: 06-1-235-9054
Fax: 06-1-269-6470
Ingyenes zöld telefon: 06-80-355-355
Ingyenes zöld fax: 06-80-344-344

India

SIGMA-ALDRICH CHEMICALS
PRIVATE LIMITED
Telephone
Bangalore: 91-80-5112-7272
New Delhi: 91-11-5165 4255
Mumbai: 91-22-2570 2364
Hyderabad: 91-40-5584 5488
Fax
Bangalore: 91-80-5112-7473
New Delhi: 91-11-5165 4266
Mumbai: 91-22-2579 7589
Hyderabad: 91-40-5584 5466

Ireland

SIGMA-ALDRICH IRELAND LTD.
Free Tel: 1800 200 888
Free Fax: 1800 600 222
Tel: 353 1 4041900
Fax: 353 1 4041910

Israel

SIGMA-ALDRICH ISRAEL LTD.
Free Tel: 1-800-70-2222
Tel: 08-948-4100
Fax: 08-948-4200

Italy

SIGMA-ALDRICH S.r.l.
Telefono: 02 33417310
Fax: 02 38010737
Numero Verde: 800-827018

Japan

SIGMA-ALDRICH JAPAN K.K.
Tokyo Tel: 03 5796 7300
Tokyo Fax: 03 5796 7315

Korea

SIGMA-ALDRICH KOREA
Tel: 031-329-9000
Fax: 031-329-9090

Malaysia

SIGMA-ALDRICH (M) SDN. BHD
Tel: 603-56353321
Fax: 603-56354116

Mexico

SIGMA-ALDRICH QUÍMICA, S.A. de C.V.
Free Tel: 01-800-007-5300
Free Fax: 01-800-712-9920

The Netherlands

SIGMA-ALDRICH CHEMIE BV
Tel Gratis: 0800-0229088
Fax Gratis: 0800-0229089
Tel: 078-6205411
Fax: 078-6205421

New Zealand

SIGMA-ALDRICH PTY., LIMITED
Free Tel: 0800 936 666
Free Fax: 0800 937 777
Tel: 61 2 9841 0500
Fax: 61 2 9841 0500

Norway

SIGMA-ALDRICH NORWAY AS
Tel: 23 17 60 60
Fax: 23 17 60 50

Poland

SIGMA-ALDRICH Sp. z o.o.
Tel: 061 829 01 00
Fax: 061 829 01 20

Portugal

SIGMA-ALDRICH QUÍMICA, S.A.
Free Tel: 800 202180
Free Fax: 800 202178
Tel: 21 9242555
Fax: 21 9242610

Russia

SIGMA-ALDRICH RUS, LLC
Tel: +7 (095) 621-5828/6037
Fax: +7 (095) 975-4792

Singapore

SIGMA-ALDRICH PTE. LTD.
Tel: 65-67791200
Fax: 65-67791822

South Africa

SIGMA-ALDRICH
SOUTH AFRICA (PTY) LTD.
Free Tel: 0800 1100 75
Free Fax: 0800 1100 79
Tel: 27 11 979 1188
Fax: 27 11 979 1119

Spain

SIGMA-ALDRICH QUÍMICA S.A.
Free Tel: 900 101376
Free Fax: 900 102028
Tel: 91 661 99 77
Fax: 91 661 96 42

Sweden

SIGMA-ALDRICH SWEDEN AB
Tel: 020-350510
Fax: 020-352522
Outside Sweden Tel: +46 8 7424200
Outside Sweden Fax: +46 8 7424243

Switzerland

SIGMA-ALDRICH CHEMIE LLC
Swiss Free Call: 0800 80 00 80
Tel: +41 81 755 2828
Fax: +41 81 755 2815

United Kingdom

SIGMA-ALDRICH COMPANY LTD.
Free Tel: 0800 717181
Free Fax: 0800 378785
Tel: 01747 833000
Fax: 01747 833313
SAFC (UK): 01202 712305

United States

SIGMA-ALDRICH
P.O. Box 14508
St. Louis, Missouri 63178
Toll-free: 800-325-3010
Call Collect: 314-771-5750
Toll-Free Fax: 800-325-5052
Tel: 314-771-5765
Fax: 314-771-5757

Internet

sigma-aldrich.com



ALDRICH[®]

P.O. Box 355
Milwaukee, WI 53201
USA



Order/Customer Service 1-800-325-3010 • Fax 1-800-325-5052
Technical Service 1-800-325-5832 • sigma-aldrich.com/techservice

Development/Bulk Manufacturing Inquiries SAFC[™] 1-800-244-1173

World Headquarters • 3050 Spruce St., St. Louis, MO 63103 • (314) 771-5765

We are committed to the success of our Customers, Employees and Shareholders through leadership in Life Science, High Technology and Service.

The SIGMA-ALDRICH Family  SIGMA  ALDRICH  Fluka  Riedel-de Haen  SUPELCO  ISOTEC[™]

©2005 Sigma-Aldrich Co. All rights reserved.
SIGMA, SAFC, SAFC[™], SIGMA-ALDRICH, ISOTEC, ALDRICH, FLUKA, and SUPELCO are trademarks belonging to Sigma-Aldrich Co. and its affiliate Sigma-Aldrich Biotechnology L.P. Riedel-de Haen[®]: trademark under license from Riedel-de Haen GmbH. Sigma products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich, Inc. warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product(s) for their particular use. Additional terms and conditions may apply. Please see reverse side of the invoice or packing slip. ReagentPlus is a registered trademark of Sigma-Aldrich Biotechnology, L.P. Thermolyne is a registered trademark of Barnstead/Thermolyne Corp. Prices subject to change.



SIGMA-ALDRICH