

Contents

Chapter 1	Synthesis and Property Measurements of Thermoelectric Materials	1
	<i>Paz Vaqueiro</i>	
1.1	Introduction	1
1.2	Synthesis	3
1.2.1	High-temperature Synthesis	3
1.2.2	Mechanochemical Synthesis	7
1.2.3	Single-crystal Growth	10
1.2.4	Solvothermal Synthesis	13
1.2.5	Colloidal Synthesis	15
1.2.6	Precursor Methods	19
1.3	Consolidation	20
1.3.1	Hot Pressing	22
1.3.2	Spark-plasma Sintering	23
1.3.3	Hot Forging	24
1.3.4	Other Consolidation Approaches	26
1.4	Property Measurements	26
1.4.1	Electrical Conductivity and Resistivity	27
1.4.2	Seebeck Coefficient	30
1.4.3	Hall Effect Measurements	34
1.4.4	Thermal Conductivity	36
1.4.5	Direct Measurement of ZT	40
1.5	Conclusions	42
	References	43

Inorganic Materials Series No. 9

Inorganic Thermoelectric Materials: From Fundamental Concepts to Materials Design

Edited by Anthony V. Powell

© The Royal Society of Chemistry 2022

Published by the Royal Society of Chemistry, www.rsc.org

Chapter 2	Theoretical Foundations and Modelling of Inorganic Thermoelectric Materials	53
	<i>N. A. Mecholsky, R. Al Rahal Al Orabi and M. Fornari</i>	
2.1	Introduction	53
2.2	Phenomenology of Thermoelectric Transport	59
2.2.1	Drude–Sommerfeld Model	59
2.2.2	Considerations on the Carrier Concentration	69
2.2.3	Anharmonic Phonon Gas	70
2.2.4	The Thermoelectric Conundrum	73
2.3	Electronic Structure and Electronic Transport	74
2.4	Vibrational Properties and Thermal Transport	81
2.5	Computational Considerations	88
2.6	Theory <i>Versus</i> Experiments	89
2.7	Conclusions	93
	References	95
Chapter 3	Nanostructuring Effects in Bulk Thermoelectrics and Their Composites	97
	<i>Min Ho Lee, Pooja Rawat and Jong-Soo Rhyee</i>	
3.1	Introduction	97
3.1.1	Nanostructured Thermoelectric Materials	99
3.1.2	Nanostructured Thermoelectric Bulk Nanocomposites	101
3.1.3	Different Approaches for New Thermoelectric Nanocomposites	114
3.2	Synthetic Strategies for Nanostructured Bulk Thermoelectric Materials	116
3.2.1	Ball Milling and Hot Pressing Methods	117
3.2.2	Wet-chemical and Spark-plasma Sintering Methods	118
3.3	Thermoelectric Properties of Ag ₂ Te–Sb ₂ Te ₃ Composites	120
3.4	Thermoelectric Properties of Size- and Shape-dependent Bi _{0.5} Sb _{1.5} Te ₃ –Ag ₂ Te Bulk Nanocomposites	126
3.5	Thermoelectric Properties of PbTe–Ag ₂ Te Bulk Composites	131
3.6	Charge-selective Anderson Localisation and Enhancement of Thermoelectric Performance in Bi-doped PbTe–Ag ₂ Te Composites	135

<i>Contents</i>	xi
3.7 Conclusions	146
Conflicts of Interest	147
References	147
Chapter 4 High-performance Thermoelectric Energy Conversion Based on Lead-free Group IV–VI Metal Chalcogenides	157
<i>Sushmita Chandra, Manisha Samanta and Kanishka Biswas</i>	
4.1 Introduction	157
4.2 Germanium Chalcogenides	160
4.2.1 Germanium Telluride (GeTe)	160
4.2.2 Germanium Selenide (GeSe)	175
4.3 Tin Chalcogenides	181
4.3.1 Tin Telluride (SnTe)	181
4.3.2 Tin Selenide (SnSe)	193
4.3.3 Tin Diselenide (SnSe ₂)	203
4.3.4 Tin Sulfide (SnS)	205
4.4 Future Outlook	205
Conflicts of Interest	207
References	207
Chapter 5 Intermetallic Thermoelectrics – Design and Preparation of Half-Heuslers, Skutterudites and Zintl-type Materials	216
<i>Jan-Willem G. Bos</i>	
5.1 Introduction	216
5.2 Recent Developments in Half-Heusler Thermoelectrics	218
5.2.1 Introduction	218
5.2.2 XNiSn (X = Ti, Zr and Hf)	221
5.2.3 XCoSb (X = Ti, Zr and Hf) and ZrCoBi	228
5.2.4 X'FeSb (X' = V, Nb, Ta)	231
5.2.5 X' _{0.8+x} CoSb (X' = V, Nb, Ta)	232
5.2.6 RNiSb (R = Sc, Y, Lanthanide)	234
5.2.7 MgAgSb for Low-temperature Applications	235
5.3 Recent Developments in Skutterudite Thermoelectrics	237
5.3.1 Introduction	237
5.3.2 Electropositive Rattlers	239
5.3.3 Group 13 Rattlers (In, Ga and Tl)	246
5.3.4 Group 14 Rattlers (Si, Ge, Sn and Pb)	248

5.3.5	Group 16 Rattlers (S, Se and Te)	249
5.3.6	Group 17 Rattlers (Br and I)	251
5.3.7	Mixed Anion Skutterudites	253
5.3.8	Phosphide Skutterudites	255
5.4	Recent Developments in Zintl-type Thermoelectric Materials	256
5.4.1	Introduction	256
5.4.2	14-1-11 Phases	258
5.4.3	1-2-2 AM_2X_2 Phases	259
5.4.4	A_2MX_2 Phases	263
5.4.5	5-2-6, 3-1-3 and 9-4-9 Phases	265
5.5	Conclusions	267
	References	269
	Subject Index	284