

Contents

Introduction *xi*

- 1 Crystal Structure and Phase Transitions in Layered Crystals of Ternary Phosphorous Chalcogenides *1***
 - 1.1 Ferrielectric, Antiferroelectric, and Modulated Orderings in $MM'P_2X_6$ (M – Cu, Ag; M' – In, Bi; X – S, Se) *1*
 - 1.2 Relaxor and Dipole Glassy States on the Phase Diagram of $CuInP_2(Se_xS_{1-x})_6$ Mixed Crystals *3*
 - 1.2.1 XRD Investigations of $CuInP_2Se_6$ *4*
 - 1.2.2 Relaxor Phase in Mixed $CuInP_2(S_xSe_{1-x})_6$ Crystals *7*
 - 1.2.3 Dipolar Glass Phase in Mixed $CuInP_2(S_xSe_{1-x})_6$ Crystals *10*
 - 1.2.4 Influence of a Small Amount of Selenium to Phase-Transition Dynamics in $CuInP_2S_6$ Crystals *12*
 - 1.2.5 Phase Diagram *13*
 - 1.3 Antiferromagnetic Ordering and Anisotropy of Magnetization in Multiferroics $Cu(In_{1-x}Cr_x)P_2S_6$ *15*
 - 1.3.1 Temperature Dependence of the Magnetization *17*
 - 1.3.2 Field Dependence of the Magnetization and Anisotropy of Magnetization and Susceptibility *19*
 - 1.4 Magnetic Ordering in $Mn_2P_2S_6$ Crystal *21*
 - 1.5 Polar Layered Crystals of SnP_2S_6 Type *30*
 - References *34*
- 2 Electronic Band Structure *41***
 - 2.1 Chemical Bonding in $P_2S(Se)_6$ Structural Groups *41*
 - 2.2 Hybridization of the Electronic Valence Orbitals and Structural Stability of $MM'P_2S(Se)_6$ -Type Compounds *43*
 - 2.3 Second-Order Jahn–Teller Effect and Dipole Ordering in $Cu(Ag)InP_2S(Se)_6$ Crystals with $d^{10} Cu^+$ and Ag^+ Cations *63*
 - 2.4 Second-Order Jahn–Teller Effect and Phase Transitions in $Cu(Ag)BiP_2S(Se)_6$ Crystals with a Stereoactive Electronic Lone Pair of Bi^{3+} *79*
 - References *85*

3	Optical Properties of $MM'P_2S(Se)_6$ Crystals	95
3.1	DFT Calculated Electronic Band Structures and Optical Parameters	95
3.2	Temperature Dependence of the Optical Absorption for $Mn_2P_2S_6$, $AgInP_2S_6$, $CuInP_2S(Se)_6$, and $CuCrP_2S_6$, SnP_2S_6 Layered Crystals	103
3.3	Appearance of Dipole Glassy State in the Edge Optical Absorption of $CuInP_2(Se_xS_{1-x})_6$ Mixed Crystals	121
	References	127
4	Phonon Spectra of Layered $MM'P_2S(Se)_6$ Crystals	131
4.1	DFT Calculated Phonon Spectra in Different Phases	131
4.2	Raman Spectroscopy of $CuInP_2S_6$ Crystal Across Ferrielectric Phase Transition	144
4.3	Phonon Spectra of $CuInP_2(Se_xS_{1-x})_6$ Mixed Crystals	151
4.4	Anisotropy of Thermal Conductivity Temperature Dependence in $Cu(Ag)In(Bi)P_2S(Se)_6$ Layered Crystals	160
4.5	Heat Capacity Anomalies at Dipole and Magnetic Ordering in $CuInP_2S(Se)_6$ and $CuCrP_2S_6$ Crystals	180
4.6	Spin-Phonon Coupling in $Mn_2P_2S_6$ Crystal	186
	References	196
5	Semiconductor to Metal Transitions in SnP_2S_6- and $Sn_2P_2S_6$-Type Compounds	201
5.1	Layered GeP_2S_6 , GeP_2Se_6 , GeP_2Te_6 , SnP_2S_6 , SnP_2Se_6 , and SnP_2Te_6 Polar Crystals with Pressure- or Chemical Composition-Induced Semiconductor–Metal Transition	201
5.2	Pressure-Induced Metal State in $Sn_2P_2S_6$ and $Sn_2P_2Se_6$ Compounds	208
5.3	DFT Calculated Transformation of Electron and Phonon Spectra at Transition into Polar Metal State	211
	References	220
6	Dielectric and Ferroelectric Properties of Layered Phosphorus Chalcogenide Crystals	223
6.1	Anisotropy Effects in Thick-Layered $CuInP_2S_6$ and $CuInP_2Se_6$ Crystals	223
6.2	Dipole Glass State in $Cu(In_xCr_{1-x})P_2S_6$ Crystals	226
6.2.1	Phase Transitions in $CuCrP_2S_6$ and $CuIn_{0.1}Cr_{0.9}P_2S_6$ Crystals	227
6.2.2	Inhomogeneous Ferrielectrics	228
6.2.3	Dipole Glass State in Mixed $CuIn_xCr_{1-x}P_2S_6$ Crystals	234
6.2.4	Phase Diagram of the Mixed $CuIn_xCr_{1-x}P_2S_6$ Crystals	236
6.3	Nonlinear Dielectric Response of Layered $(Ag,Cu)(In,Cr)P_2S_6$ Crystals	237
6.4	Dielectric Spectroscopy of $CuBiP_2Se_6$ Crystals	244
6.4.1	Antiferroelectric Phase Transition	244
6.4.2	Freezing Phenomena	246
	References	248

- 7 Ionic Conductivity and Low-Frequency Noise Spectroscopic Studies 251**
- 7.1 Ionic Conductivity Investigations in CuInP_2S_6 and $\text{CuIn}_{1+\delta}\text{P}_2\text{S}_6$ Crystals 251
- 7.2 Conductivity Spectroscopy of $\text{AgInP}_2(\text{Se}_x\text{S}_{1-x})_6$ and $(\text{Cu}_x\text{Ag}_{1-x})\text{CrP}_2\text{S}_6$ Crystals 252
- 7.3 Low-Frequency Noise Spectroscopy of Layered CuInP_2S_6 253
- 7.3.1 Intrinsic Noise Types 254
- 7.3.2 Experimental Techniques for Noise Determination 255
- 7.3.3 Noise Spectroscopy in Materials Science 256
- 7.3.4 Brief Overview of Low-Frequency Noise Spectroscopic Studies of CuInP_2S_6 256
- 7.4 Electrical Conductivity of Layered $\text{CuInP}_2(\text{S}_x\text{Se}_{1-x})_6$ Crystals 258
- References 259
- 8 Ultrasonic and Piezoelectric Studies of Phase Transitions in Two-Dimensional CuInP_2S_6 -Type Crystals 263**
- 8.1 Ultrasonic Investigation of Phase Transition in CuInP_2S_6 Crystals 263
- 8.2 Piezoelectric and Ultrasonic Investigations of Mixed $(\text{Ag,Cu})\text{InP}_2(\text{S,Se})_6$ Layered Crystals 265
- 8.3 Ultrasonic Spectroscopy of Quasi Two-Dimensional $\text{CuInP}_2(\text{Se}_x\text{S}_{1-x})_6$ Mixed Crystals 268
- 8.4 Piezoelectric and Elastic Properties of Layered Materials of $\text{Cu}(\text{In,Cr})\text{P}_2(\text{S,Se})_6$ System 270
- References 272
- 9 Nano Scale Investigations, Domain Structure, and Switching Processes of Low-Dimensional Ferroelectric Layered Chalcogenides 275**
- 9.1 Ferrielectric State in Few Layer or Monolayer CuInP_2S_6 Samples 275
- 9.2 Bright Domain Walls in $\text{CuInP}_2\text{Se}_6$ Crystals 283
- 9.3 Antisite Defects in Layered Multiferroic $\text{CuCr}_{0.9}\text{In}_{0.1}\text{P}_2\text{S}_6$ 287
- References 291
- 10 Phenomenological Description of Soft Phonon Spectra, Phase Diagrams, and Domain Morphology of Low-Dimensional Ferroelectric Layered Chalcogenides 295**
- 10.1 Brief Overview 295
- 10.2 Spatially Modulated Incommensurate Phases and Soft Phonon Dispersion in Ferroelectric Layered Chalcogenides 296
- 10.2.1 Landau–Ginzburg–Devonshire-Free Energy Functional and Lagrange Function 297
- 10.2.2 The Stability of Spatially Modulated Phases in Ferroelectric Chalcogenides 301
- 10.2.3 Analytical Description of the Soft Phonon Dispersion 302

- 10.2.4 Analysis of the Critical Points in the Soft Phonon Spectra 305
- 10.2.5 The Behavior of Soft Acoustic Phonons in the Vicinity of Critical Wave Vectors 306
- 10.2.6 Elastic Softening of the Sound Velocity 307
- 10.2.7 Soft Phonon Dispersion in Ferroelectric Chalcogenides: Comparison with Experiment 308
- 10.2.8 Temperature Dependence of Static Dielectric Susceptibility 309
- 10.3 Phase Diagrams with Incommensurate Phases and Domain Splitting in Thin Films of Ferroelectric Layered Chalcogenides 311
- 10.3.1 Approximate Analytical Solution of the Linearized Euler–Lagrange Equations 313
- 10.3.2 Phase Equilibrium and Domain Structure Temperature Evolution 314
- 10.4 Phenomenological Description of Phase Diagrams and Complex Domain Morphology of Ferroelectric Layered Chalcogenide Nanoparticles 317
- 10.4.1 Reconstruction of CIPS Thermodynamic Potential from Experiments 318
- 10.4.2 Temperature–Stress Phase Diagrams of Bulk CuInP_2S_6 319
- 10.4.3 The Stress-Induced Phase Transitions in CuInP_2S_6 Nanoparticles of Different Shapes 322
- 10.4.4 Labyrinthine Domains in CIPS Nanoparticles 325
- 10.4.5 Analytical Description of Complex Domain Morphology in Ferroelectric Layered Chalcogenide Nanoparticles 327
- 10.5 Phenomenological Description of Bright-Contrast and Dark-Contrast Domain Walls in Ferroelectric–Antiferroelectric Layered Chalcogenides 332
- 10.5.1 LGD–FSM Approach 332
- 10.5.2 Phase Diagrams of the Order Parameters 335
- 10.5.3 Bright and Dark Domain Walls 337
- 10.5.4 Comparison with Experiment 339
- 10.6 Conclusions 341
- 10.A Appendix A: Analytical Expressions for the Soft Phonon Frequency 342
- 10.B Appendix B: Soft Acoustic Mode Behavior in the Vicinity of Critical Wave Vectors 345
- 10.C Appendix C: Temperature Dependence of the Static Dielectric Susceptibility 346
- 10.D Appendix D: Derivation of PE–SDFE Transition Temperature for Spherical Nanoparticles 347
- 10.E Appendix E: Derivation of PE–PDFE Transition Temperature for Spherical Nanoparticles 349
- References 352

- 11 Application Examples of Ferroelectric 2D Layered Indium Copper Thiophosphate Chalcogenide, CuInP_2S_6 359**
- 11.1 The Ferroelectric (FE) Family of Metal (M) Hypo(tio/seleno)diphosphates 359

11.2	Piezoelectric and Pyroelectric Activity and Electrocaloric Effectivity of CuInP ₂ S ₆ Nanoflakes	360
11.2.1	Piezoactivity of CuInP ₂ S ₆ Nanoflakes	360
11.2.2	Pyroactivity of CuInP ₂ S ₆ Nanoflakes	360
11.2.3	Electrocaloric Performances of CuInP ₂ S ₆ Nanoflakes	361
11.3	Promises of 2D Layered CuInP ₂ S ₆ for Ferroelectric Field Effect Transistors and Memory Applications	361
11.3.1	Theoretical Considerations and Evaluations	362
11.3.2	Experimental Investigations and Propositions	362
11.3.3	Negative Capacitance Field Effect Transistors Based on Two-Dimensional van der Waals Heterostructures	364
11.4	Conclusions	365
	References	366
	Index	371

