

2014, Volume 189, pag. 1-50

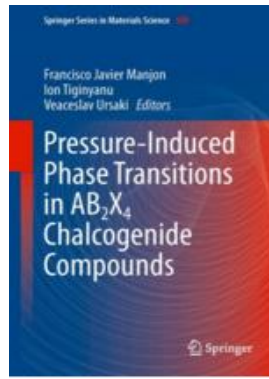
# Relation of $A^{II}B_2^{III}X_4^{VI}$ Compounds to Other Materials, Their Properties and Applications (Instead of Introduction)

V. V. Ursaki, I. M. Tiginyanu

[https://doi.org/10.1007/978-3-642-40367-5\\_1](https://doi.org/10.1007/978-3-642-40367-5_1)

## Abstract

This chapter provides a review of  $A^{II}B_2^{III}X_4^{VI}$  compounds as a class of materials in a wide family of ternary compounds. The origin and the place of these materials in the hierarchy of ternary compounds are presented. The technological methods for the growth of these compounds are analyzed and the procedures for obtaining larger crystals for practical applications are evidenced. The crystal structure and the energy band structure are discussed in terms of the production of spinel, layered, or tetragonal structure according to the number of octahedral and tetrahedral cationic sites. The “ordered-vacancy compounds” are analyzed taking into account different degrees of possible disorder. The relationship of the electronic band structures of these compounds with the band structure of their parent chalcopyrite compounds  $A^IB^{III}X_2^{VI}$  and their grand parent  $A^{II}B^{VI}$  compounds is clarified. The influence of the crystallographic structure upon the energy band structure is evidenced by comparing crystal modifications with different space groups. Optical, radiative, and vibrational properties are discussed and the energy level scheme explaining the extrinsic optical properties of  $A^{II}B_2^{III}X_4^{VI}$



2014, Volume 189, pag. 1-50

semiconductors is presented. It is shown that a source of interest in  $A^{II}B_2^{III}X_4^{VI}$  compounds is their crystal structures derived from the diamond type, but modified to accommodate three or more atoms of different sizes, allowing additional symmetries and thus an increase in the selection of electro-optic, acousto-optic, and non-linear materials for device applications. Another source of interest related to the variety of  $A^{II}B_2^{III}X_4^{VI}$  crystal structures comes from their importance for the investigation of the role of structure and composition in a response to the applied pressure.

### References:

1. Hahn H, Frank G, Klinger W, Meyer AK, Storger G (1953) Untersuchungen über ternäre Chalkogenide. V. Über einige ternäre Chalkogenide mit Chalkopyritstruktur. *Z Anorg Allg Chem* 271:153–170
2. Goodman CHL, Douglas RW (1954) New semiconducting compounds of diamond type structure. *Physica* 20:1107–1109
3. Bernard M (1975) Glances at ternary compounds. *J de Physique. Colloque C3*, 36(Suppl 9):C3–C1
4. Shay JL, Wernick JH (1975) Ternary chalcopyrite semiconductors, growth, electronic properties and applications. Pergamon Press, Oxford
5. Goryunova NA (1963) Chemistry of diamond-like semiconductors. Leningrad State University, Leningrad
6. Goryunova NA, Ryvkin SM, Fishman IM, Spenkor GI, Yarosketskii ID (1969) Second harmonic generation in ternary semiconductors. *Sov Phys Semicond* 2:1272
7. Berkovskii FM, Goryunova NA, Orlov VM, Ryvkin SM, Sokolova VI, Tsvetkova EV, Shpenkov GP (1969) CdSnP 22 laser excited with an electron beam. *Sov Phys Semicond* 2:1027
8. Chemla DS, Kupecek Ph, Robertson DS, Smith RC (1971) Silver thiogallate, a new material with potential for infrared devices. *Opt Commun* 3:29–31
9. Parthe E (1975) Crystal chemistry of tetrahedral structures. Gordon and Breach, London
10. Pamplin R (1960) Super-cell structure of semiconductors. *Nature* 188(4745):136–137
11. Razzetti C, Lottici PP, Antonioli G (1987) Structure and lattice Structure and lattice dynamics of nonmagnetic defective  $A^{II}B^{III}X_4^{VI}$  compounds and alloys. *Prog Crystal Growth Charact* 15:43–73



2014, Volume 189, pag. 1-50

12. Hahn H, Frank G, Klingler W, Storger A-D, Storger G (1955) Untersuchungen über ternäre Chalkogenide. VI. Über Ternäre Chalkogenide des Aluminiums, Galliums und Indiums mit Zink, Cadmium und Quecksilber. *Z Anorg Allg Chem* 279:241–270
13. Agostinelli E, Gastaldi L, Viticoli S (1985) Crystal growth and X-ray structural investigation of two forms of  $\text{HgGa}_2\text{Te}_4$ . *Mat Chem and Phys* 12:303–312
14. Mocharnyuk GF, Babyuk TI, Derid OP, Lazarenko LS, Markus MM, Radautsan SI (1977) Order-disorder transition in  $\text{CdGa}_2\text{Se}_4$  -  $\text{CdIn}_2\text{Se}_4$  solid solutions. *Sov Phys Dokl* 22:749
15. Razzetti C, Lottici PP, Zanotti L (1984) Ternary and pseudoternary  $\text{AB}_2\text{X}_4$  compounds (  $\text{A}=\text{Zn}, \text{Cd}$ ;  $\text{B}=\text{Ga}, \text{In}$ ;  $\text{X}=\text{S}, \text{Se}$ ). *Mat Chem Phys* 11:65–83
16. Bernard JE, Zunger A (1988) Ordered-vacancy-compound semiconductors: pseudocubic  $\text{CdIn}_2\text{Se}_4$ . *Phys Rev B* 37:6835–6856
17. Binsma JJM, Galing LJ, Bloem J (1981) Order-disorder behaviour and tetragonal distortion of chalcopyrite compounds. *Phys Stat Sol (a)* 63:595–603
18. Tiginyanu IM, Ursaki VV, Fulga VN (1989) On the order-disorder phase transition in the cation sublattice of  $\text{ZnGa}_2\text{Se}_4$ . *Fiz Tekn Poluprov* 23:1725–1727
19. Dietrich M, Unterricker M, Deicher M, Burchard A, Magerle R, Pfeiffer W, Forkel-Wirth D, Tiginyanu IM, Moldovyan NA (1996) Quadrupole interaction in defect chalcopyrite semiconductors studied by PAC. *Cryst Res Technol* 31:853–857
20. Dietrich M, Unterricker M, Deicher M, Burchard A, Magerle R, Pfeiffer W, Forkel-Wirth D, Tiginyanu IM, Moldovyan NA (1996) PAC investigation of ordered vacancy semiconductors II-III. *Hyperfine Interact (C)* 1:242–246
21. Phillips JC (1973) Bonds and bands in semiconductors. Academic, New York
22. Neumann H (1983) About the average bond ionicity in  $\text{AIBIIICVI}_2\text{AIBIIIC}_2\text{VI}$  compounds. *Cryst Res Technol* 18:1391–1396
23. Kumar V (1987) Bond ionicity and susceptibility in  $\text{AIBIIICVI}_2\text{AIBIIIC}_2\text{VI}$  compounds. *Phys Chem Sol* 48:827–831
24. Ursaki VV, Burlakov II, Tiginyanu IM, Raptis YS, Anastassakis E, Anedda A (1999) Phase transitions in defect chalcopyrite compounds under hydrostatic pressure. *Phys Rev B* 59:257–268
25. Lottici PP, Parisini A, Razzetti C, Carra P (1984) Effective ionic charges in  $\text{CdGa}_2\text{Se}_4$  and  $\text{CdGa}_2\text{S}_4$ . *Solid State Commun* 51:691–695
26. Wakamura K, Arai T (1981) Empirical relationship between effective ionic charges and optical dielectric constants in binary and ternary cubic compounds. *Phys Rev B* 24:7371–7379
27. Kushwaha AK, Kushwaha SS (2005) Effective charges in ternary chalcogenide spinels. *Indian J Pure Appl Phys* 43:664–667
28. Nitsche R (1975) Crystal chemistry, growth and properties of multi-cation chalcogenides. *J de Physique. Colloque C3, 36(Suppl 9):C3–C9*



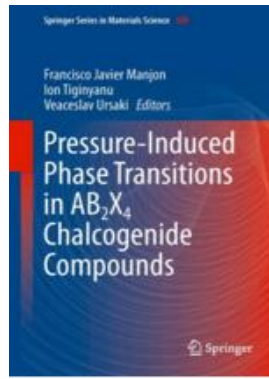
2014, Volume 189, pag. 1-50

29. Nitsche R (1971) Crystal growth and phase investigations in multi-component systems by vapour transport. *J Cryst Growth* 9:238–243
30. Bohac P, Gaumann A (1974) New fluxes for crystal growth of chalcogenides. *J Cryst Growth* 26:171–173
31. Yamamoto N, Miyauchi T (1972) Growth of single crystals of  $\text{CuGaS}_2$  and  $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$  in solution. *Japan J Appl Phys* 11:1383–1384
32. Schafer H (1964) Chemical transport reactions. Academic Press, New York
33. Nitsche R, Bolsterli HU, Lichtensteiger M (1961) Crystal growth by chemical transport reactions-I: binary, ternary, and mixed-crystal chalcogenides. *J Phys Chem Solids* 21:199–205
34. Scholz H, Kluckow R (1967) In: Peiser HC (ed) *Crystal growth*. Pergamon Press, Oxford, p 475. Proceedings of the international conference on Crystal Growth, Boston, Mass, 20–24 June 1966
35. Paorice C, Zanotti L, Zuccalli G (1978) A temperature variation method for the growth of chalcopyrite crystals by iodine vapour transport. *J Crystal Growth* 43:705–710
36. Curti M, Gastaldi L, Lottici PP, Paorici C, Razzetti C, Viticoli S, Zanotti L (1987) Synthesis and characterization of the  $\text{ZnxCd}_{1-x}\text{In}_2\text{S}_4$  pseudoternary solid solution. *J Solid State Chem* 69:289–298
37. Badikov VV, Matveev IN, Pshenichnikov SM, Rychik OV, Trotsenko NK, Ustinov ND, Shcherbakov SI (1980) Growth and nonlinear properties of  $\text{HgGa}_2\text{S}_4$ . *Sov J Quantum Electron* 10:1300–1302
38. Feigelson RS, Route RK (1984) Crystal growth and optical properties of  $\text{CdGa}_2\text{S}_4$ . *Prog Crystal Growth Charact* 10:189–197
39. Mooser E, Pearson WB (1957) The chemical bond in semiconductors. *J Electron* 1:629–645
40. Mooser E (1983) Crystal chemistry and classification of multinary semiconductors. *Nuovo Cimento* 2D:1613–1627
41. Mooser E, Pearson WB (1959) On the crystal chemistry of normal valence compounds. *Acta Crystallogr* 12:1015–1022
42. Philips JC (1970) Ionicity of the chemical bond in crystals. *Rev Mod Phys* 42:317–356
43. Van Vechten JA (1969) Quantum dielectric theory of electronegativity in covalent systems I. electronic dielectric constant. *Phys Rev* 182:891–905
44. Razzetti R, Lottici PP (1983) Preparation and Raman spectroscopy of  $\text{ZnxCd}_{1-x}\text{In}_2\text{S}_4$  mixed cation layered compounds. *Nuovo Cimento* 2D:2044–2049
45. Haeuseler H (1979) X-ray investigations in the system  $\text{CdIn}_2\text{S}_4$ – $\text{CdIn}_2\text{Se}_4$ . *J Solid St Chem* 29:121–123
46. Antonioli G, Lottici PP, Parisini A, Razzetti C (1984) EXAFS study of mixed crystals of the  $\text{AIIIBIII}_2\text{XVI}_4\text{AIIIB}_2\text{IIIX}_4\text{VI}$  family. *Prog Crystal Growth Charact* 10:9–18
47. Burdett JK, Price GD, Price SL (1982) Role of the crystal-field theory in determining the structure of spinels. *J Am Chem Soc* 104:92–95



2014, Volume 189, pag. 1-50

48. Meloni F, Shaukat A (1984) Classification of the  $AB_2C_4AB_2C_4$  spinels: a pseudopotential orbital radii approach. *Prog Crystal Growth Charact* 10:37–43
49. Zunger A (1980) Structural stability of 495 binary compounds. *Phys Rev Lett* 44:582–586
50. Andreoni W, Baldereschi A, Biemont E, Phillips JC (1979) Hard-core pseudopotentials and structural maps of solids. *Phys Rev B* 20:4814–4823
51. Jiang X, Lambrecht WRL (2004) Electronic band structure of ordered vacancy defect chalcopyrite compounds with formula II-III 22 -VI 44. *Phys Rev B* 69:035201
52. Ozaki S, Muto K, Adachi S (2003) Optical properties and electronic band structure of  $CdGa_2Te_4$ . *J Phys Chem Sol* 64:1935–1939
53. Singh P, Verma UP, Jensen P (2011) Electronic and optical properties of defect chalcopyrite  $HgAl_2Se_4$ . *J Phys Chem Sol* 72:1414–1418
54. Chizhikov VI, Panyutin VL, Ponedelnikov BE, Rozencon AE (1981) Structure de bande lectronique de  $CdAl_2Te_4$  dans les modifications avec les groupes spatiaux  $D_{112d}D_{2d11}$ ,  $D_{92d}D_{2d9}$ ,  $D_{12d}D_{2d1}$  et  $S_{24}S_{42}$ . *Phys Stat Sol B* 106:91–98
55. Baldereschi A, Meloni F, Aymerich F, Mula G (1977) Electronic band structure of cubic spinel  $CdIn_2S_4$ . *Inst Phys Conf Ser* 35:193–200
56. Kambara T, Oguchi T, Gondaira KI (1980) Electronic band structures of semiconducting ferromagnetic spinels  $CdCr_2S_4$  and  $CdCr_2Se_4$ . *J Phys C Solid St Phys* 13:1493–1512
57. Oguchi T, Kambara T, Gondaira KI (1980) Self-consistent electronic structures of magnetic semiconductors by a discrete variational  $X\alpha X\alpha$  calculation. I. Ferromagnetic spinels,  $CdCr_2S_4$  and  $CdCr_2Se_4$ . *Phys Rev B* 22:872–879
58. Oguchi T, Kambara T, Gondaira KI (1981) Self-consistent electronic structures of magnetic semiconductors by a discrete variational  $X\alpha X\alpha$  calculation. II.  $HgCr_2Se_4$ . *Phys Rev B* 24:3441–3444
59. Guzzi M, Grilli E (1984) Localized levels and luminescence of  $AB_2X_4AB_2X_4$  semiconducting compounds. *Mater Chem Phys* 11:295–304
60. Radautsan SI, Georgobiani AN, Tiginyanu IM (1984) II-III 22 -VI 44 compounds: properties and trends for applications. *Prog Crystal Growth Charact* 10:403–412
61. Tarricone L, Zanotti L (1984) Photoconductivity and photomemory in  $ZnxCd_{1-x}In_2S_4$  layered crystals. *Mater Chem Phys* 11:161–176
62. Gentile AL (1984) Devices using ternary or multinary compounds. *Prog Crystal Growth Charact* 10:241–256
63. Levine BF, Bethea CG, Kasper HM, Thiel FA (1976) Nonlinear optical susceptibility of  $HgGa_2S_4$ . *IEEE J Quant Electron* QE-12:367–368
64. Ren D, Huang J, Qu Y, Hu X, Zhang L, Andreev Yu, Geico P, Badikov V, Lanski G, Tikhomirov A (2003) Optical properties and  $CO_2$  laser SHG with  $HgGa_2S_4$ . *Chinese Optics Lett* 1:613–615



2014, Volume 189, pag. 1-50

65. Ren D, Huang J, Hu X, Qu Y, Andreev YM, Geico PP, Badikov VV (2004) Efficient  $\text{CO}_2$  frequency doubling with  $\text{Hg}_{1-x}\text{Cd}_x\text{Ga}_2\text{S}_4$ . Proc SPIE 5397:205–211
66. Zunger A (1987) Order-disorder transformation in ternary tetrahedral semiconductors. Appl Phys Lett 50:164–166
67. Rincon C (1992) Order-disorder phase transition in ternary chalcopyrite compounds and pseudobinary alloys. Phys Rev B 45:12716–12719
68. Yamanaka T, Takeuchi Y, (1983) Order-disorder transition in  $\text{MgAl}_2\text{O}_4$  spinel at high temperatures up to 1700 °C. Z Kristallographie Cryst Mater 165:65–78
69. Cynn H, Sharma SK, Cooney TF, Nicol M (1992) High-temperature Raman investigation of order-disorder behavior in the  $\text{MgAl}_2\text{O}_4$  spinel. Phys Rev 45:500–502
70. De Ligny D, Neuville DR, Flank A-M, Lagarde P (2009) Structure of spinel at high temperature using in-situ XANES study at the Al and Mg K-edge. J Phys Conf Ser 190:012178
71. Navrotsky A, Kasper RB (1976) Spinel disproportionation at high pressure: calorimetric determination of enthalpy of formation of  $\text{Mg}_2\text{SnO}_4$  and  $\text{Co}_2\text{SnO}_4$  and some implications for silicates. Earth Planet Sci Lett 31:247–254
72. Petrov K, Tsolovski I (1980) On the high temperature spinel-ramsdellite transformation of lithium titanate  $(\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4)$ . Phys Stat Sol A 58(1):K85–K88
73. Tang XC, Huang BY, He YH (2006) Phase transition of lithiated-spinel  $\text{Li}_2\text{Mn}_2\text{O}_4$  at high temperature. Trans Nonferrous Metals Soc China 16:438–445
74. Sekine T, Mitsuhashi T (2001) High-temperature metastability of cubic spinel  $\text{Si}_3\text{N}_4$ . Appl Phys Lett 79:2719