

# Supporting information: “Mechanochemical Synthesis of Sustainable Ternary and Quaternary Nanostructured $\text{Cu}_2\text{SnS}_3$ , $\text{Cu}_2\text{ZnSnS}_4$ , and $\text{Cu}_2\text{ZnSnSe}_4$ Chalcogenides for Thermoelectric Applications”

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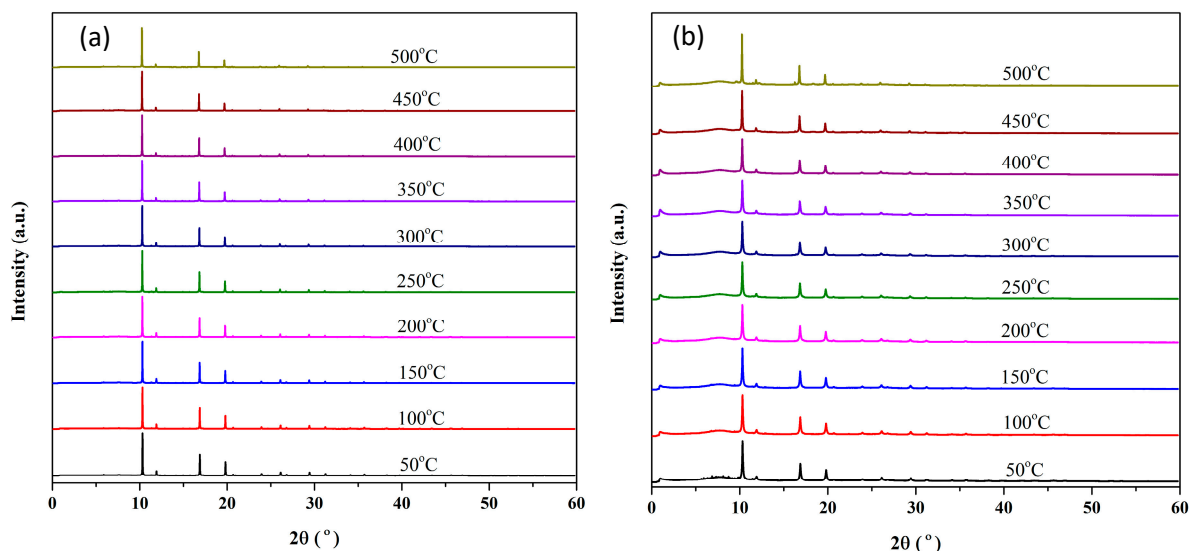
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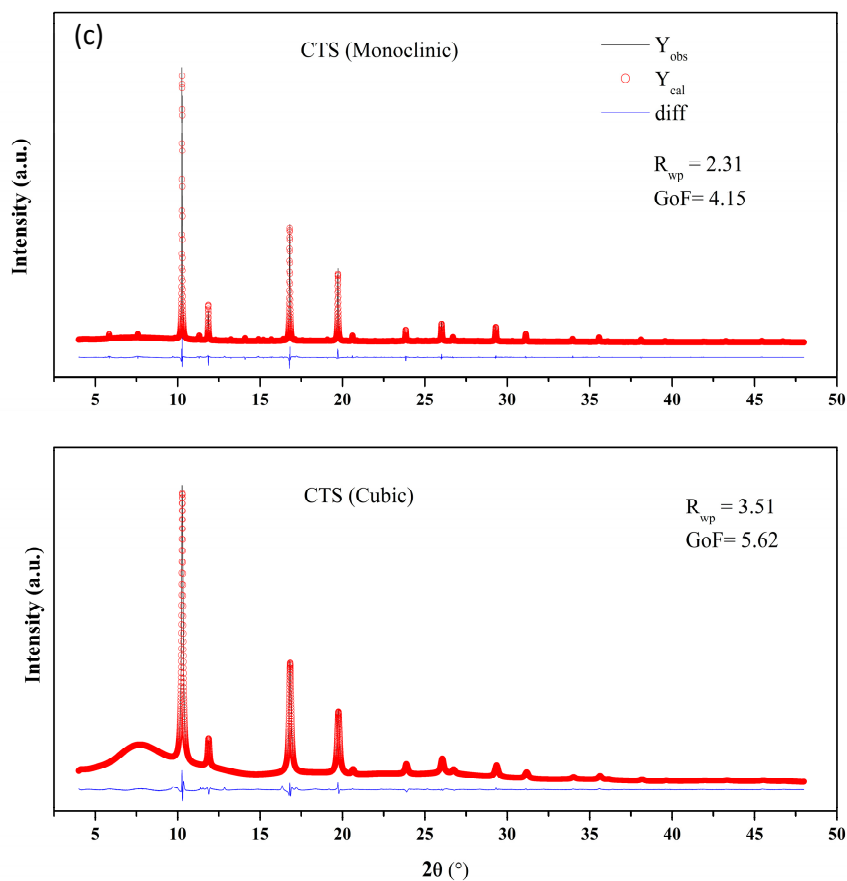
<sup>3</sup> Department of Physics, University of Genova, via Dodecaneso 33, 16146 Genova, Italy; putti@fisica.unige.it (M. P.)

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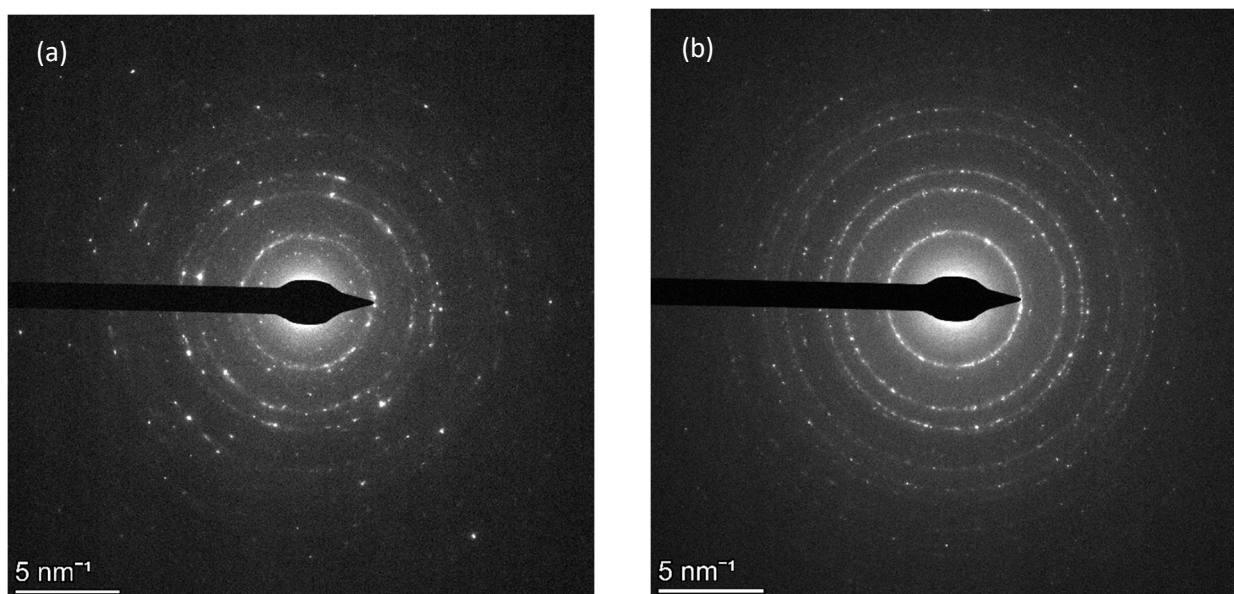
<sup>5</sup> Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439 USA; lrebuffi@anl.gov (L. R.)

\*Correspondence: paolo.scardi@unitn.it (P.S)

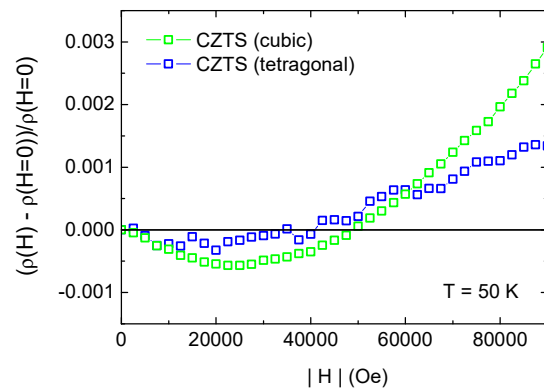




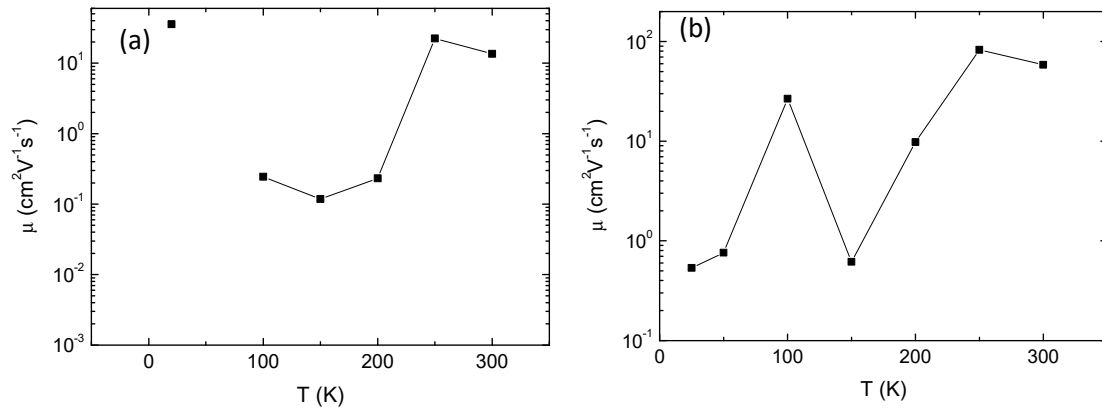
**Figure S1.** Temperature dependent SXRD measurement on CTS Ordered (a) and disordered cubic (b) Rietveld refinement performed on ordered and disordered CTS XRD data collected at 350°C, where  $Y_{obs}$ ,  $Y_{cal}$ , and  $diff$  are collected, calculated and difference, respectively. The value of  $R_{wp}$  and  $GoF$  for other patterns were similar to the values observed here.



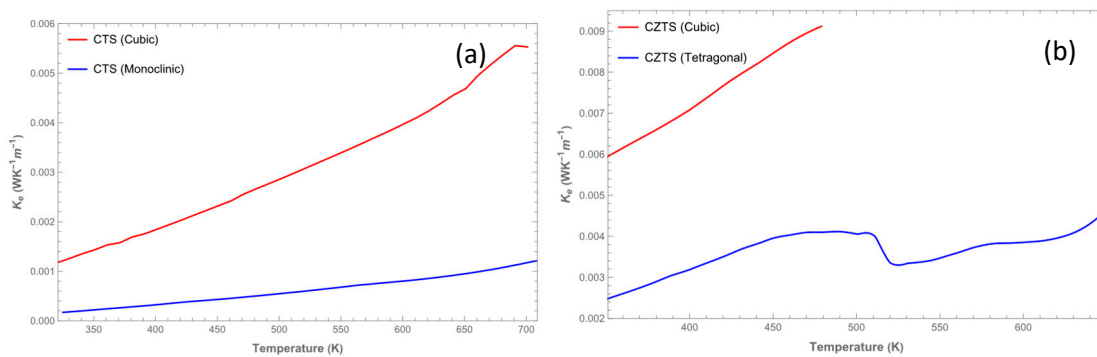
**Figure S2.** SAED patterns for of (a) Monoclinic CTS and (b) Disordered Cubic CTS. It is evident from SAED the inner Debye-Scherrer rings are missing for Disordered Cubic CTS representing,  $(11-1)$ ,  $(021)$ .

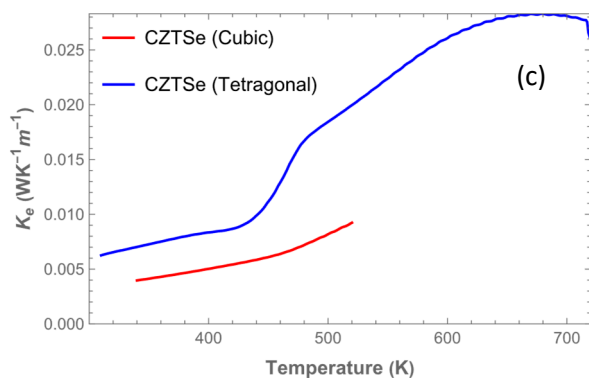


**Figure S3.** Magnetoresistivity  $(\rho(H)-\rho(H=0))/\rho(H=0)$  of (a)Tetragonal CZTS and (b)Disordered Cubic CZTS, measured at  $T=50$ K



**Figure S4.** Temperature-dependent mobility measurement of (a)Tetragonal CZTS and (b)Disordered Cubic CZTS





**Figure S5.** Temperature-dependent electronic part of the thermal conductivity according to the Wiedemann-Franz law:  $k_e = L \sigma T$  and  $L = 1.5 + \exp[-|S|/116]$ , where  $L$  in  $10^{-8} \text{ W}\Omega\text{K}^{-2}$  and  $S$  in  $\mu\text{V}/\text{K}$  of (a) CTS, (b) CZTS and (c) CZTSe

**The relaxed disordered structure of CTS, CZTS, CZTSe used for calculating electronic properties:**

**Disordered CTS-1**

```

1.0000000000000000
11.0521121791927346 0.0000000000000000 0.0000000000000000
0.0000000000000000 11.0521121791927346 0.0000000000000000
0.0000000000000000 0.0000000000000000 10.8937928306091436

```

Cu Sn S

21 11 32

**Direct**

```

0.0000000000000000 0.0000000000000000 0.0000000000000000
0.0000000000000000 0.5000000000000000 0.5000000000000000
0.5000000000000000 0.0000000000000000 0.0000000000000000
0.5000000000000000 0.0000000000000000 0.5000000000000000
0.5000000000000000 0.5000000000000000 0.0000000000000000
0.0065877668834062 0.2494657375125300 0.2493503885705550
0.9934122331165938 0.2494657375125300 0.7506495894294432
0.9934122331165938 0.7505342404874682 0.2493503885705550
0.0065877668834062 0.7505342404874682 0.7506495894294432
0.4955536083830125 0.2456471866824401 0.2442584608331799
0.5044463916169875 0.2456471866824401 0.7557415171668183
0.5044463916169875 0.7543527913175581 0.2442584608331799
0.4955536083830125 0.7543527913175581 0.7557415171668183

```

0.2543528133175599 0.0044463916169875 0.2442584608331799  
0.2543528133175599 0.9955536083830125 0.7557415171668183  
0.2505342624874700 0.4934122331165938 0.2493503885705550  
0.2505342624874700 0.5065877668834062 0.7506495894294432  
0.7456471646824383 0.9955536083830125 0.2442584608331799  
0.7456471646824383 0.0044463916169875 0.7557415171668183  
0.7494657155125282 0.5065877668834062 0.2493503885705550  
0.7494657155125282 0.4934122331165938 0.7506495894294432  
0.2596844621631647 0.2403155378368353 0.0103606080958940  
0.5000000000000000 0.5000000000000000 0.5000000000000000  
0.2504241060030381 0.2495758939969619 0.4857781070091676  
0.2596844621631647 0.7596844401631628 0.9896393919041060  
0.0000000000000000 0.0000000000000000 0.5000000000000000  
0.0000000000000000 0.5000000000000000 0.0000000000000000  
0.2504241060030381 0.7504240840030363 0.5142218929908324  
0.7403155158368335 0.2403155378368353 0.9896393919041060  
0.7495758719969601 0.2495758939969619 0.5142218929908324  
0.7403155158368335 0.7596844401631628 0.0103606080958940  
0.7495758719969601 0.7504240840030363 0.4857781070091676  
0.1171186533837769 0.1166593468268360 0.1312780176361912  
0.1312117352836921 0.1287421006623646 0.6438808800029676  
0.1287428317454484 0.6287428427454458 0.1379182782776454  
0.1161747671528701 0.6161747781528675 0.6323817662968025  
0.6173330956472540 0.1173330846472496 0.1312581415774261  
0.6160926606036625 0.1160926496036652 0.6327858692597914  
0.6166593578268333 0.6171186643837743 0.1312780176361912  
0.6287421116623619 0.6312117462836895 0.6438808800029676  
0.3833406421731667 0.3828813356162257 0.1312780176361912  
0.3712578883376381 0.3687882537163105 0.6438808800029676  
0.3826669043527531 0.8826669043527460 0.1312581415774261  
0.3839073393963375 0.8839073393963375 0.6327858692597914  
0.8712571572545542 0.3712571572545542 0.1379182782776454

0.8838252218471325 0.3838252218471325 0.6323817662968025  
0.8828813356162257 0.8833406421731667 0.1312780176361912  
0.8687882537163105 0.8712578883376381 0.6438808800029676  
0.3839073393963375 0.1160926496036652 0.3672141307402086  
0.3826669043527531 0.1173330846472496 0.8687418474225765  
0.3712578883376381 0.6312117462836895 0.3561191199970324  
0.3833406421731667 0.6171186643837743 0.8687219713638115  
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0.8838252218471325 0.6161747781528675 0.3676182337031975  
0.8712571572545542 0.6287428427454458 0.8620817107223573  
0.1161747671528701 0.3838252218471325 0.3676182337031975  
0.1287428317454484 0.3712571572545542 0.8620817107223573  
0.1312117352836921 0.8712578883376381 0.3561191199970324  
0.1171186533837769 0.8833406421731667 0.8687219713638115  
0.6287421116623619 0.3687882537163105 0.3561191199970324  
0.6166593578268333 0.3828813356162257 0.8687219713638115  
0.6160926606036625 0.8839073393963375 0.3672141307402086  
0.6173330956472540 0.8826669043527460 0.8687418474225765

**Disordered CTS -2**

1.00000000000000

10.9835867451454678 0.0065491028448356 0.0009814362662756

0.0065526745611678 10.9677768328474130 -0.0024228570139087

0.0010179507687051 -0.0024167454741761 10.8860105502243059

Cu Sn S

22 10 32

**Direct**

0.7435685556643321 0.2446968819169157 0.0041217695757183

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0.4950139957390860 0.9962206345633362 0.4951509148606590

0.4942271211489242 0.4938199366316383 0.0055678920589770  
0.0013926521937009 0.2538029530014754 0.2478419194496908  
0.9980019083681029 0.2543316382039151 0.7543656271207979  
0.9973385364906093 0.7464714348152910 0.2552426669239338  
0.0025075019488909 0.7466033898410132 0.7462845783076801  
0.4991992832325707 0.2508368137942583 0.2334080524773796  
0.5057419011817643 0.5038181883661395 0.4944777228299770  
0.5007584605910864 0.7492819490516140 0.2513205525899167  
0.4995284272443143 0.7495338404298835 0.7493538408581486  
0.2570071424266374 0.0037192426521102 0.2453515811649112  
0.2580853298360495 0.0023254150816001 0.7511182526688742  
0.2569535020154703 0.4903214802288858 0.2499313945506429  
0.2472592967478207 0.5041351798008762 0.7554494719062319  
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0.7478670212190011 0.4990532027857313 0.2489065154359338  
0.7457959735944399 0.4935270057941921 0.7470887842392528  
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0.4996101638019894 0.2504315662132441 0.7650281738726861  
0.2540355290984380 0.2518952797691085 0.4844141181766446  
0.2652499745379515 0.7488891378932649 0.0008464834270256  
0.0000291381425725 0.9991701937626516 0.5000798875186589  
0.0000717630744234 0.4854923534793230 0.0017578989945548  
0.2616785485206350 0.7407188177539012 0.5071216034898498  
0.9999045122082464 0.0145460210909860 0.0016551760655616  
0.7473062707553026 0.2673762214139899 0.4993693327486000  
0.7346787374912012 0.7493216427452225 0.0013516293139588  
0.7383020139537066 0.7399856226154213 0.4909096000264128  
0.1340549978143528 0.1342876465495166 0.1334594827548372  
0.1283977725894232 0.1290429554712631 0.6416933756673515  
0.1266906056806150 0.6229401041911444 0.1397865745597855  
0.1198585857577470 0.6169921388968973 0.6308105492133791

0.6233068411935108 0.1268906134307386 0.1243817171049884  
0.6234526772804969 0.1130331443277868 0.6240140296163119  
0.6150050178119599 0.6153891464094770 0.1322564577017360  
0.6170626107913435 0.6166381286980354 0.6339372971520376  
0.3755322690392475 0.3751839949824571 0.1254017788197501  
0.3761177748814148 0.3898453710948147 0.6255003188677080  
0.3862912070338282 0.8830224974642817 0.1317010762695219  
0.3834708743306976 0.8824936693751440 0.6328181542683282  
0.8643909983282114 0.3660552903858019 0.1320522057262608  
0.8847053594844070 0.3834885248835462 0.6331496802257277  
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0.8681363054406148 0.8713627812938398 0.6398598132326612  
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0.8797209669640225 0.6152522962085953 0.3679572399503215  
0.8738072761436086 0.6228321685272462 0.8620479995795449  
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0.1254950046332439 0.8761089223866634 0.8619895774541888  
0.6137420140281620 0.3808276160975765 0.3610380543495424  
0.6317149213200395 0.3827892605952883 0.8858450534528615  
0.6171919591704267 0.8830278492370383 0.3664412963232451  
0.6141573732455328 0.8830072371098368 0.8682173982629777

**Disordered CZTS**

1.0000000000000000

10.9598501947749938 -0.1249688936118855 -0.0250469597288990



-0.1264099280703482 11.0295371370476118 0.0599160245040838

-0.0266992297007424 0.0589943285448715 10.9564733017760236

Cu S Sn Zn

16 32 8 8

Direct

-0.0086094871104244 0.0176019928789748 0.0117549950930625

0.0090637146023007 0.2352502945225316 0.2442983543228030

0.2519913800031896 0.0010761620424628 0.2293020463628186

0.2578110899270293 0.2425376417484607 0.0071856777315485

0.5055444549312837 0.0087513312314706 -0.0050207994653725

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0.7450902021245014 0.0105312736137847 0.2441231575854355

0.2749409967710221 0.4825828966669199 0.2545952145691507

0.5041277520780681 0.4934953567697137 0.0059100783374260

0.5017242725523329 0.2506881612351941 0.7596217941554511

0.4987621315182707 0.7384779576387808 0.2431939258425500

0.2567947091579703 0.4943562604149025 0.7489053991486825

0.7089156552464573 0.0298179275070346 0.7951281032453403

0.2613657800872393 0.7365082915164167 0.4881509654337615

0.7279242928526070 0.7592402338527421 0.0065134723735166

0.5023810985469183 0.7520523617004569 0.7527793530047897

0.1292307306114943 0.1248291587797668 0.1231173487096321

0.8582225198463291 0.8882966436471226 0.1177559404151297

0.8715737497316159 0.1317061201648548 0.8848040958879474

0.1205469013176373 0.8864227558364931 0.8854606233643103

0.1257763875853987 0.3706340300176075 0.3601018101993681

0.8660021087242816 0.1367047288531414 0.3652970192603400

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0.8908844311307138 0.5941529315359718 0.3560297375382636  
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0.3793142359457686 0.6208553031333763 0.3677613452099204  
0.3879301966280820 0.3796843626157975 0.6354503614079504  
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-0.0288205276717870 -0.0265704735298441 0.4935267675538384  
-0.0038473263255956 0.4826124869901982 -0.0092737099485521  
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0.2780977478281365 0.7534045053416784 -0.0115128294749623  
0.4975135940376536 0.0035902897243571 0.5065838326826306  
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0.7366223715453758 0.2472979067323166 -0.0026134053218011

0.0146711917529684 0.4883593532612543 0.4993240360651845  
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0.5049232186432423 0.5050213394497090 0.4893310213440047  
0.7392817277840106 0.4961200839872347 0.7478692961089842

### Disordered CZTSe

1.0000000000000000

11.5425481796000007 0.0000000000000000 0.0000000000000000

0.0000000000000000 11.5425481796000007 0.0000000000000000

0.0000000000000000 0.0000000000000000 11.4796619414999999

Zn Cu Sn Se

8 16 8 32

### Direct

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0.7885054766415179 0.0197334048102722 0.7767899936972557

0.7504048020837797 0.4731830684685432 0.7626170461669387

-0.0002245688588903 0.5039881058245593 -0.0361886831754705

0.5227258441157406 0.2460077514205972 0.7465011424643688

0.4841748675610680 -0.0031048166907927 0.4995015729188517

-0.0152165144976480 0.2227417128942303 0.2987379338530981

0.2570610931783207 0.5006121507794857 0.7555467864263200

0.2613140059321787 -0.0090551011556622 0.2659546795135315

0.2479312396849483 0.5249042869776248 0.2332651093603103

0.7318171950626275 0.0120786324328238 0.2471355636304772

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0.5090695457999829 0.0138956736322157 -0.0007445266523149

0.4977304945926022 0.4973056392376395 0.0004543864368630

-0.0077295613414229 0.2701858301136066 0.7360211233338299

-0.0253620671837388 0.7537899720249825 0.7624373799370725  
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