Multifunctional Cu$_2$TSiS$_4$ (T = Mn and Fe): Polar Semiconducting Antiferromagnets with Nonlinear Optical Properties

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ABSTRACT: Cu$_2$TSiS$_4$ (T = Mn and Fe) polycrystalline and single-crystal materials were prepared with high-temperature solid-state and chemical vapor transport methods, respectively. The polar crystal structure (space group $Pmn2_1$) consists of chains of corner-sharing and distorted CuS$_4$, Mn/FeS$_4$, and SiS$_4$ tetrahedra, which is confirmed by Rietveld refinement using neutron powder diffraction data, X-ray single-crystal refinement, electron diffraction, energy-dispersive X-ray spectroscopy, and second harmonic generation (SHG) techniques. Magnetic measurements indicate that both compounds order antiferromagnetically at 8 and 14 K, respectively, which is supported by the temperature-dependent (100−2 K) neutron powder diffraction data. Additional magnetic reflections observed at 2 K can be modeled by magnetic propagation vectors k = (1/2,0,1/2) and k = (1/2,1/2,1/2) for Cu$_2$MnSiS$_4$ and Cu$_2$FeSiS$_4$, respectively. The refined antiferromagnetic structure reveals that the Mn/Fe spins are canted away from the ac plane by about 14°, with the total magnetic moments of Mn and Fe being 4.1(1) and 2.9(1) μ_B, respectively. Both compounds exhibit an SHG response with relatively modest second-order nonlinear susceptibilities. Density functional theory calculations are used to describe the electronic band structures.
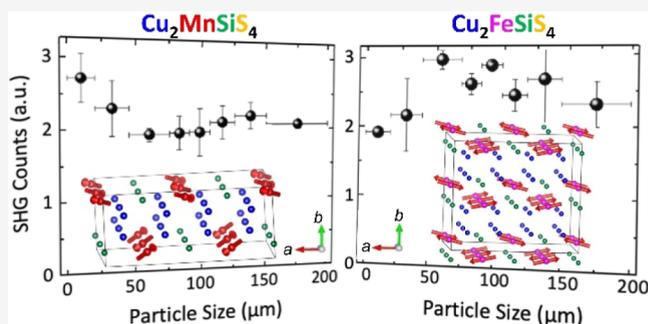
INTRODUCTION

Cu$_2$TMS$_4$ (T = Mn, Fe, Co, Ni, Cu, Zn, Cd, and Hg; M = Si, Ge, and Sn), simplified as CTMS, and related quaternary chalcogenides are important semiconductors that have various optoelectronic and energy-related applications such as nonlinear optics,[1] solar cell technology,[2,3] gamma-ray detectors,[4] supercapacitors,[5] and thermoelectric materials.[6−8] CTMS compounds adopt either the tetragonal stannite ($I\bar{4}2m$),[9] tetragonal kesterite ($I\bar{4}$),[10] tetragonal pseudo-cubic ($P\bar{4}$),[11] or orthorhombic wurtz-stannite ($Pmn2_1$) structure types.[12] While the three tetragonal structure types are nonpolar, wurtz-stannite (WSt) possesses a polar crystal structure. The most common crystal structure type for CTMS compounds is stannite (St), for example, Cu$_2$FeSnS$_4$, which is a super-structure derived from sphalerite (Sp) such at $a_{St} \sim a_{Sp}$, $c_{St} \sim 2 a_{Sp}$.[12] The polar WSt crystal structure is a superstructure of wurtzite (W) via doubling of the unit cell along the a axis ($a_{WSt} \sim 2 a_w$; $b_{WSt} \sim \sqrt{3} a_w$; $c_{WSt} \sim c_w$), with the same metal-sulfur coordination environment as in St.[12] The only CTMS compounds reported thus far with the polar WSt crystal structure are Cu$_2$MnGeS$_4$ and Cu$_2$TSiS$_4$ (T = Mn and Fe).[12]

Most reported CTMS compounds are semiconducting antiferromagnets with antiferromagnetic (AFM) ordering transitions at low temperatures. Cu$_2$MnGeS$_4$ shows AFM ordering near 8 K and adopts a magnetic space group P_ac with a magnetic propagation vector k = (1/2,0,1/2), and spins are antiferromagnetically coupled in a collinear arrangement.[13] The same magnetic propagation vector k = (1/2,0,1/2) is also observed in Cu$_2$MnSnS$_4$ and Cu$_2$FeGeS$_4$ (space group $I\bar{4}2m$),[14,15] but the collinear AFM magnetic structure (the magnetic space group is P_a2_1) in Cu$_2$MnSnS$_4$ is different from that in Cu$_2$MnGeS$_4$,[14] and the final magnetic model of Cu$_2$FeGeS$_4$ is not determined.[15] Cu$_2$TSiS$_4$ (T = Mn and Fe) are reported as antiferromagnets with a Néel temperature (T_N) of 8 and 15 K, respectively, and predicted to be multiferroic materials,[16,17] but the magnetic structures remain unexplored. For multiferroic materials, an understanding of magnetic structures is important. Since different magnetic structures have been observed in the CTMS family, it would be interesting to reveal the magnetic structures in Cu$_2$TSiS$_4$ (T = Mn and Fe).
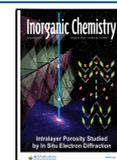
CTMS belongs to the large family of $AB^{II}M^{IV}X_4$ (A = alkali metals, Cu, and Ag; B = alkaline earth metals, transitional metals, Pb, and Eu; M = Si, Ge, and Sn; X = O, S, Se, and Te) compounds, which are also good candidates for nonlinear optical (NLO) materials. For example, Cu_2MnGeS_4 exhibits a strong SHG response with second-order NLO susceptibility, $\chi_S^{(2)} \sim 16.9$ pm/V, at room temperature.[1] Similarly, Li_2CdGeS_4, with the same WSt crystal structure, shows a robust SHG response with $\chi^{(2)} \sim 22.5$ pm/V.[18,19] Cu_2TSiS_4 (T = Mn and Fe) were determined to adopt polar crystal structures based on X-ray single crystal (for T = Mn) or powder (for T = Fe) diffraction data.[12,20] However, the definitive confirmation of the polar crystal structures and NLO properties has not yet been investigated.

In this study, we use X-ray powder diffraction (XRPD), neutron powder diffraction (NPD), and transmission electron microscopy (TEM) techniques to confirm the reported polar crystal structure of Cu_2TSiS_4 (T = Mn and Fe). Here, we also report the magnetic properties, magnetic structures, optical transparency in the infrared region, and second-order NLO properties of Cu_2TSiS_4 (T = Mn and Fe) by magnetic measurements, temperature-dependent NPD, attenuated total reflectance (ATR), Fourier transform infrared (FT-IR) spectroscopy, and second-order NLO property measurements, respectively. We perform density functional theory calculations to reveal the detailed electronic band structures.

■ EXPERIMENTAL SECTION

Starting Materials and Synthesis. Cu_2TSiS_4 (T = Mn and Fe) samples were prepared by heating the mixture of Cu (99.999% mass fraction, Alfa Aesar), Si (99.999% mass fraction, Alfa Aesar), and S (99.5% mass fraction, Alfa Aesar) powders with either Mn (99.95% mass fraction, Alfa Aesar) or Fe (99.99% mass fraction, Alfa Aesar) powders that were thoroughly ground and pressed into a pellet (6 mm in diameter). All sample preparations were carried out inside an argon-filled glove box with an O_2 and H_2O concentration of less than 1 ppm. Each pellet was then loaded into a quartz tube that was sealed under a dynamic vacuum ($<10^{-3}$ Torr). The obtained ampoule was heated in a box furnace at 600 °C for 1 d and 900 °C for 3 d with heating and cooling rates of 100 and 150 °C/h, respectively, which is a modified heating profile based on the previous report.[12] Cu_2TSiS_4 (T = Mn and Fe) single crystals ($<1 \times 1.5 \times 0.3$ mm^3) were grown via the chemical vapor transport (CVT) method with iodide as the transport agent. For the CVT method, the mixture of elements was heated with a similar heating profile as the solid-state method but with a longer dwelling time (5 d) at 900 °C.

X-ray and Neutron Powder Diffraction. Room-temperature laboratory XRPD patterns for the polycrystalline samples were collected with a scattering angle 2θ ranging from 10 to 70° for 30 min using a Rigaku Miniflex-600 benchtop X-ray powder diffractometer (Cu K$_\alpha$, λ = 1.5418 Å). NPD data were collected for ~3 g of the microcrystalline Cu_2TSiS_4 (T = Mn and Fe) samples using a powder diffractometer POWGEN at the Spallation Neutron Source, Oak Ridge National Laboratory.[21] A neutron band with a center wavelength of 2.67 Å was used to collect the data. NPD data were obtained at various temperatures between 100 and 2 K. Rietveld refinements and data analysis using the NPD data were carried out by employing the suite of FullProf programs.[22] Magnetic structure symmetry analysis was performed with the computational tools at the Bilbao crystallographic server.[23]

X-ray Single-Crystal Diffraction. X-ray single-crystal diffraction data for Cu_2TSiS_4 (T = Mn and Fe) were obtained at room temperature on a Rigaku XtaLAB Synergy-i diffractometer with a HyPix-Bantam direct photon-counting detector and Mo K$_\alpha$ radiation. Small single crystals were mounted on a loop and measured on the goniometer head of the diffractometer. Data reduction and absorption correction were carried out using the Rigaku CrysAlis^{Pro} package. The

crystal structure of Cu_2TSiS_4 (T = Mn and Fe) was solved with the space group $Pmn2_1$ and refined using the SHELX-2018 software.[24] A summary of data collection and refined structure parameters is presented in Table S1. The corresponding atomic positions and anisotropic thermal parameters are provided in Tables S2 and S3.

Transmission Electron Microscopy. TEM experiments were conducted with a probe-aberration-corrected sub-Å resolution JEOL JEM-ARM200cF microscope using an accelerating voltage of 200 kV. Polycrystalline Cu_2TSiS_4 (T = Mn and Fe) powders were crushed into thin, electron-transparent pieces, which were transferred onto a carbon-coated 200-mesh Cu TEM grid. For the Cu_2FeSiS_4 sample, a few single crystals were also used to prepare thin pieces in a similar way to that used for the Cu_2TSiS_4 (T = Mn and Fe) powder samples. Selected area electron diffraction (SAED) patterns were obtained along the [100] or [001] direction on a single-crystal piece, and the corresponding atomic resolution high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected.

Chemical Analysis. Elemental analysis of Cu_2TSiS_4 (T = Mn and Fe) was performed on single crystals with an Octane Elect Plus energy-dispersive X-ray (EDX) spectroscopy system, an accessory of a JEOL JSM-IT500HRLV scanning electron microscope (SEM). The SEM images and elemental maps were collected with an accelerating voltage of 15 kV.

Magnetic Measurements. Cu_2TSiS_4 (T = Mn and Fe) powders were loaded in a plastic capsule inside a plastic straw for the magnetic property measurements with the quantum design DynaCool physical property measurement system. Zero-field-cooled (ZFC) and field-cooled (FC) protocols were used to measure the magnetic susceptibility between 1.8 and 300 K with an applied magnetic field (H) of 0.1 T. Isothermal field-dependent magnetization was measured at 1.8 and 300 K using H ranging ±9 T.

Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy. Optical transparency data were collected with 256 scans from 400 to 4000 cm^{-1} using a Thermo Nicolet 380 FT-IR spectrometer with an ATR accessory. The OMNIC software was used to collect and analyze the spectra. This method, where a diamond crystal is in optical contact with the samples, results in the thickness-dependent effect on the intensity of the spectra being negligible.[25] This is due to the penetration depth into the sample approaching the lower limit of the particle size, approximately 2 μm, within the sample.

Second-Order NLO Property Measurements. Crystalline Cu_2TSiS_4 (T = Mn and Fe) powders were sieved into discrete particle size ranges of <20, 20−45, 45−75, 75−90, 90−106, 106−125, 125−150, and >150 μm by employing a collection of stainless-steel W.S. Tyler test sieves and a Gilson sieve shaker in order to investigate the phase-matching (PM) nature of the SHG of the samples. Each sample was enclosed in a glass capillary tube by flame sealing under the vacuum to prevent moisture and air exposure to the samples during measurements. The capillary tubes were mounted on a homemade sample holder, and the measured SHG efficiencies of the samples were compared to those of the optical-quality reference materials, $AgGaS_2$ (AGS) and $AgGaSe_2$ (AGSe), for the estimation of the second-order nonlinear susceptibility, $\chi^{(2)}$. Note that the particle size ranges for the AGS and AGSe benchmark materials obtained from G&H Cleveland are a bit dissimilar to those of the samples, but this does not influence our NLO property analysis.

SHG measurements were recorded at room temperature using an input wavelength of λ = 1800 nm. Coherent light with λ = 1064 nm was first generated by an EKSPLA PL-2250 series diode-pumped Nd:YAG laser with a pulse width of 30 ps and a repetition rate of 50 Hz to generate tunable pulses. The Nd:YAG laser pumped an EKSPLA Harmonics Unit H400, where the input beam frequency was tripled to 355 nm via a series of NLO beam mixing. Two beams of 355 and 1064 nm next passed into an EKSPLA PG403-SH-DFG Optical Parametric Oscillator consisting of four components: (i) a double-pass parametric generator, (ii) a single-pass parametric amplifier, (iii) a second harmonic generator, and (iv) a difference frequency generator. A full explanation of the laser and detection setup has been provided previously.[26]
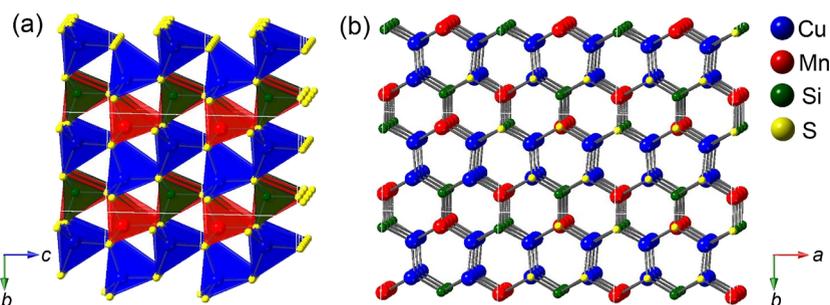
Figure 1. Perspective view of the crystal structure of Cu_2MnSiS_4 along the crystallographic a axis (a) and c axis (b).
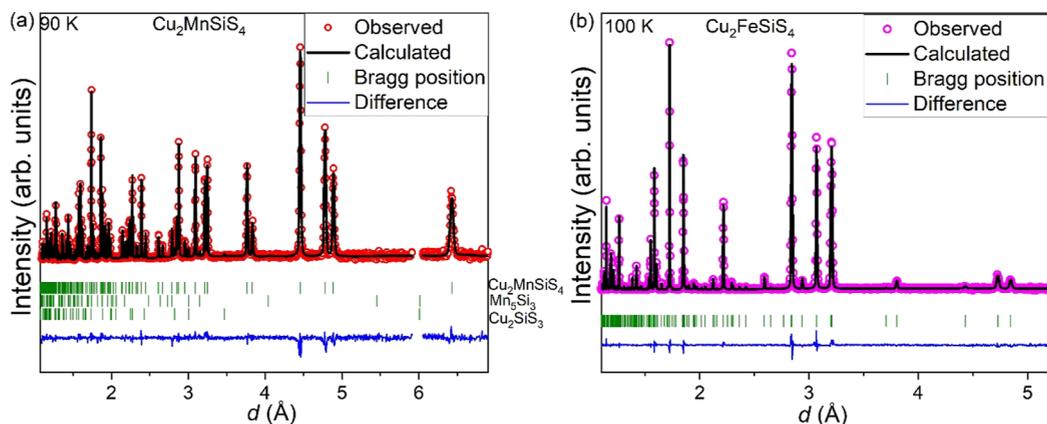
Figure 2. Rietveld refinement of Cu_2MnSiS_4 (a) and Cu_2FeSiS_4 (b) in the space group $Pmn2_1$ using NPD data. The observed data (red), the calculated pattern (black), and the difference between those two patterns (blue) are provided. The expected Bragg peak positions (green) of nuclear reflections are also depicted.

Density Functional Theory Calculations. The all-electron, full-potential linearized augmented plane-wave method implemented in WIEN2k was used to calculate the electronic structure.[27] Structural parameters were taken from NPD refinement. The Perdew−Burke−Ernzerhof generalized gradient approximation (GGA) was adopted for the exchange−correlation functional.[28] $14 \times 14 \times 22$ and $16 \times 17 \times 16$ k meshes were used in the Brillouin zone integration for Cu_2MnSiS_4 and Cu_2FeSiS_4, respectively. The muffin tin radii were chosen to be 2.37, 2.47, 2.36, 1.83, and 1.93 Bohr radii for Fe, Mn, Cu, Si, and S, respectively, and the size of a plane-wave basis set was determined from $R_{mt}K_{max}$ of 7.0, where R_{mt} is the smallest atomic muffin tin radius, and K_{max} is the largest plane-wave vector. To consider the strong correlation effect, GGA + U was adopted within the fully localized limit.[29,30] The effective on-site Coulomb interaction parameters, $U_{eff} = U − J$, of 4.0 and 5.0 eV were used for Mn-d and Fe-d orbitals, respectively.

RESULTS AND DISCUSSION

Crystal Structure. The XRPD patterns of the polycrystalline Cu_2TSiS_4 (T = Mn and Fe) samples prepared via high-temperature solid-state synthesis match the theoretical patterns calculated from the polar structure in the space group $Pmn2_1$ (Figure S1). The crystal structure of Cu_2TSiS_4 (T = Mn and Fe) is a cation-ordered, orthorhombic superstructure of the wurtzite structure. The wurtzite (ZnS) structure is built from the hexagonal closest packing of S ions, where the metal ions occupy half of the tetrahedral holes. In this structure, all cations are tetrahedrally coordinated by sulfide anions, and vice versa. As shown in the crystal structure of Cu_2MnSiS_4, the CuS_4 tetrahedra are connected via corner-sharing along the crystallographic a axis and form CuS_4 columns that are connected in a zigzag fashion along the crystallographic c axis

(Figure 1a). Similarly, MnS_4 and SiS_4 are mixed alternately to form zigzag layers between the CuS_4 layers along the b axis.

The refinements of the crystal structure of Cu_2TSiS_4 (T = Mn and Fe) were carried out using the NPD data collected at 90 and 100 K, respectively. The reported polar crystal structure of Cu_2TSiS_4 (T = Mn and Fe) in the space group $Pmn2_1$ was used as the initial model during the Rietveld refinements. However, it became apparent that a relatively small amount of other phases were detected in the Cu_2MnSiS_4 sample. Therefore, additional materials were added to the model. The final refinement indicated that Cu_2MnSiS_4 was the major phase (mass % = 96.7%), although small amounts of unwanted Mn_5Si_3 (mass % = 1.92%) and Cu_2SiS_3 (mass % = 1.38%) existed in the sample (Figure 2a). A peak near 5.9 Å was excluded because its intensity mainly stems from the magnetic contribution from the Mn_5Si_3 impurity phase, which orders antiferromagnetically with $T_N \sim 100$ K.[31] The Cu_2FeSiS_4 sample was assessed as being phase pure, as the NPD data at 100 K could be completely accounted for with the single Cu_2FeSiS_4 phase (Figure 2b).

Selected refinement parameters and fractional atomic coordinates are given in Table 1. The refined unit cell parameters of Cu_2MnSiS_4 at 90 K are slightly smaller than those refined using room-temperature single-crystal X-ray diffraction data [$a = 7.5431(1)$ Å, $b = 6.4401(1)$ Å, $c = 6.1877(1)$ Å, and $V = 300.229(8)$ Å^3] and previously reported values for Cu_2MnSiS_4 at 293 K [$a = 7.543(2)$ Å, $b = 6.446(1)$ Å, $c = 6.193(1)$ Å, and $V = 301.1(1)$ Å^3].[20] The refined unit cell parameters of Cu_2FeSiS_4 at 100 K are also close to those refined using room temperature single-crystal X-ray diffraction data [$a = 7.4162(1)$ Å, $b = 6.4121(1)$ Å, $c = 6.1397(1)$ Å, and

Table 1. Selected Structure Parameters and Refinement Details for Cu_2TSiS_4 (T = Mn and Fe) Using NPD Data

	Cu_2MnSiS_4		Cu_2FeSiS_4	
nominal composition	Cu_2MnSiS_4		Cu_2FeSiS_4	
refined formula	Cu_2MnSiS_4		Cu_2FeSiS_4	
temperature	90 K	2 K	100 K	2 K
mol. wt.g/mol	338.38		339.28	
density, g/cm³ (calculated)	3.759	3.760	3.872	3.875
space group, #	$Pmn2_1$, # 21		$Pmn2_1$, # 21	
Z	2		2	
lattice parameters	$a = 7.5264(1)$ Å, $b = 6.4250(1)$ Å, $c = 6.1823(1)$ Å, $V = 298.957(1)$ Å³	$a = 7.5262(2)$ Å, $b = 6.4237(1)$ Å, $c = 6.1817(1)$ Å, $V = 298.86(1)$ Å³	$a = 7.4119(1)$ Å, $b = 6.3985(1)$ Å, $c = 6.1352(1)$ Å, $V = 290.964(8)$ Å³	$a = 7.4115(1)$ Å, $b = 6.39656(8)$ Å, $c = 6.13509(8)$ Å, $V = 290.854(7)$ Å³
Rietveld criteria of fit of the major nuclear phase	$R_P = 3.98\%, R_{wp} = 3.17\%, R_{exp} = 1.82\%, \chi^2 = 3.04$	$R_P = 5.17\%, R_{wp} = 4.44\%, R_{exp} = 1.32\%, \chi^2 = 11.3$	$R_P = 3.27\%, R_{wp} = 2.65\%, R_{exp} = 1.48\%, \chi^2 = 3.21$	$R_P = 3.23\%, R_{wp} = 3.44\%, R_{exp} = 0.9\%, \chi^2 = 14.6$
site	Wyckoff symbol	x, y, z	x, y, z	x, y, z	x, y, z
Cu	4b	0.7528(2), 0.6781(2), 0.178(1)	0.7531(2), 0.6781(3), 0.178(1)	0.2476(2), 0.3248(3), 0.013(2)	0.2476(2), 0.3257(3), 0.012(2)
Mn (Fe)	2a	0, 0.8441(7), 0.670(3)	0, 0.842(1), 0.666(2)	0, 0.1541(3), 0.500(3)	0, 0.1548(3), 0.499(2)
Si	2a	0, 0.1748(7), 0.178(3)	0, 0.1768(9), 0.187(2)	0, 0.8298(8), 0	0, 0.8300(7), 0
S1	2a	0, 0.858(1), 0.062(1)	0, 0.860(1), 0.065(2)	0, 0.814(1), 0.350(2)	0, 0.816(1), 0.349(2)
S2	2a	0, 0.183(1), 0.515(1)	0, 0.187(1), 0.518(1)	0, 0.141(1), 0.885(2)	0, 0.141(1), 0.883(2)
S3	4b	0.7304(6), 0.6668(9), 0.550(1)	0.7313(8), 0.668(1), 0.552(1)	0.2643(8), 0.329(1), 0.388(1)	0.2651(8), 0.329(1), 0.388(1)

$V = 291.964(8)$ Å³], and published values for Cu_2FeSiS_4 at 293 K ($a = 7.404$ Å, $b = 6.411$ Å, $c = 6.14$ Å, and $V = 291.45$ Å³).[12] The unit cell volume of Cu_2MnSiS_4 is slightly larger than that of Cu_2FeSiS_4, which is because the ionic radius of the Mn^{2+} ion (0.66 Å) is larger than that of the Fe^{2+} ion (0.63 Å).[32]

As shown in Figure 1, the crystal structure of Cu_2TSiS_4 (T = Mn and Fe) consists of CuS_4, TS_4 (T = Mn and Fe), and SiS_4 tetrahedra. In each tetrahedron, Cu/Mn/Fe/Si coordinates with one S1 atom, one S2 atom, and two S3 atoms, with slightly different bond distances (d) within the respective tetrahedra (Table 2). The refined $d(Cu–S)$ and $d(Si–S)$ in the

Table 2. Selected Bond Distances in Cu_2TSiS_4 (T = Mn and Fe) Refined at 90 and 100 K, Respectively

Cu_2MnSiS_4		Cu_2FeSiS_4	
Cu/Mn/Si–S distances (Å)		Cu/Fe/Si–S distances (Å)	
Cu–S1	2.304(6)	Cu–S1	2.300(8)
Cu–S2	2.333(4)	Cu–S2	2.318(9)
Cu–S3	2.31(1)	Cu–S3	2.31(1)
Cu–S3	2.356(7)	Cu–S3	2.342(8)
Mn–S1	2.43(2)	Fe–S1	2.361(1)
Mn–S2	2.377(9)	Fe–S2	2.364(2)
Mn–S3 (×2)	2.440(8)	Fe–S3 (×2)	2.359(7)
Si–S1	2.16(1)	Si–S1	2.15(1)
Si–S2	2.08(2)	Si–S2	2.11(1)
Si–S3 (×2)	2.158(9)	Si–S3 (×2)	2.135(7)

two Cu_2TSiS_4 (T = Mn and Fe) compounds are very close in most instances or identical in some instances, considering the estimated standard deviations. As expected, $d(Mn–S)$ is longer than $d(Fe–S)$. The refined $d(Cu–S) = 2.30–2.36$ Å and $d(Mn–S) = 2.38–2.44$ Å are very close to those found in the isostructural Cu_2MnGeS_4 compound [$d(Cu–S) = 2.31–2.35$ Å and $d(Mn–S) = 2.43–2.46$ Å].[20] The obtained $d(Si–S) = 2.08–2.16$ Å is in good agreement with the $d(Si–S) = 2.14$ Å observed in Cu_2CoSiS_4 with the space group $I\bar{4}2m$.[12] Because there are four different bond distances in the CuS_4 tetrahedron and three unequal bond distances in MnS_4, FeS_4, and SiS_4 tetrahedra, all of the tetrahedra are distorted, and the chains of corner-sharing tetrahedra are unsymmetrical, as shown in Figure 1a. When looking at the projection along the crystallographic c axis, all atoms are connected in distorted hexagonal patterns, that is, honeycomb patterns containing three sulfide anions and three metal cations (Figure 1b). Such an arrangement of connected, distorted tetrahedra explains the polar crystal structure, and the more distorted CuS_4 tetrahedron contributes most to the polarization.

Electron Diffraction. To confirm the refined crystal structure of Cu_2TSiS_4 (T = Mn and Fe) obtained from NPD, TEM experiments were performed. An SAED pattern of the Cu_2MnSiS_4 sample was obtained along the [100] direction. It is consistent with the simulated pattern of Cu_2MnSiS_4 with the space group $Pmn2_1$. The (010) diffraction spot has a similar intensity as the (020) spot, and the extinct (001) spot has intensity due to the double diffraction, which is a typical phenomenon of the dynamical scattering of a thick crystal. The corresponding atomic resolution HAADF-STEM image shows rows of alternate bright and weak spots and a neighboring row of weaker spots. Because the atomic column image intensity in the HAADF-STEM image is almost proportional to the atomic number (Z^2) of an atom and the number of that atom along the column, the heavier the atom, the brighter the spots.
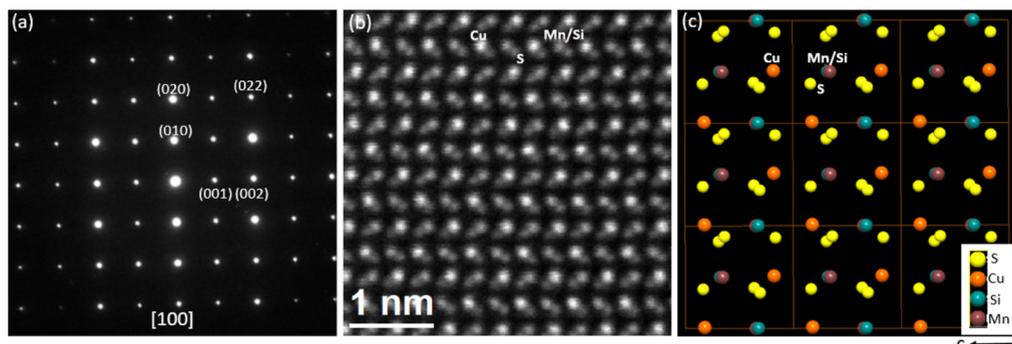
Figure 3. (a) Electron diffraction pattern along the [100] direction, (b) atomic resolution HAADF-STEM image, and (c) perspective view of the crystal structure of Cu_2MnSiS_4 with the space group $Pmn2_1$.
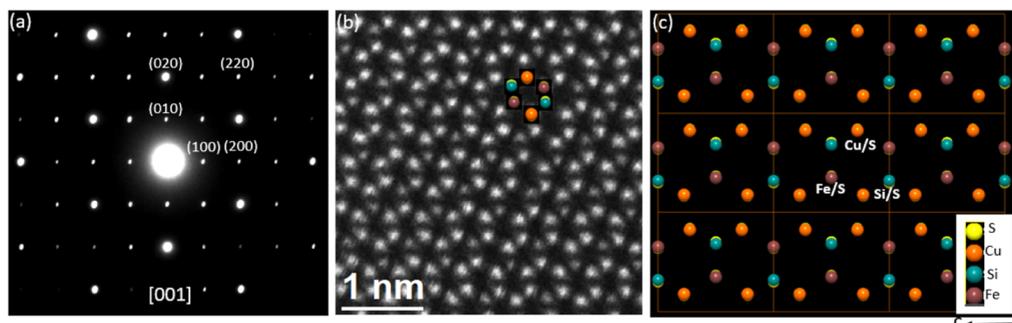
Figure 4. (a) Electron diffraction pattern along the [001] direction, (b) atomic resolution HAADF-STEM image, and (c) perspective view of the crystal structure of Cu_2FeSiS_4 with the space group $Pmn2_1$.
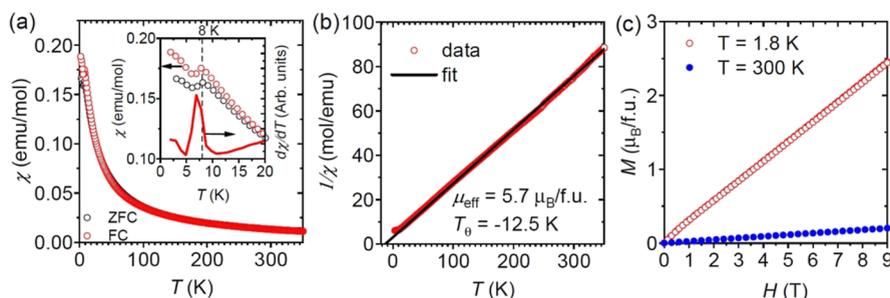
Figure 5. (a) Temperature-dependent ZFC−FC magnetic susceptibility at 0.1 T. Inset depicts the magnetic susceptibility data below 20 K (left axis) and the temperature derivative of the magnetic susceptibility (right axis), highlighting the kink that represents the magnetic phase transition. The dashed line is the guide to the eye for 8 K. (b) Inverse magnetic susceptibility fit with the Curie−Weiss law, and (c) field-dependent magnetization of polycrystalline Cu_2MnSiS_4.

Therefore, the intensity of Cu ($Z = 29$) is the brightest, the mixed columns of Mn ($Z = 25$) and Si ($Z = 14$) have an average atomic number of 19.5 and are less bright, and S columns ($Z = 16$) are the weakest. In Figure 3b, rows with alternate bright and weak spots are the rows of Cu atoms and Si/Mn atoms in the crystal structure of Cu_2MnSiS_4 with the space group $Pmn2_1$ (Figure 3c). The adjacent rows with weaker spots in Figure 3b correspond to the S atoms in the crystal structure (Figure 3c).

The electron diffraction pattern recorded from a single piece of Cu_2FeSiS_4 can be indexed to the [001] direction with the space group $Pmn2_1$ (Figure 4a). The extinct (100) spot that has intensity is due to double diffraction. The corresponding atomic resolution HAADF-STEM image shows a pattern consisting of hexagonal spots, which correspond well with the crystal structure viewed along the [001] direction (Figure 4b,c). Along this projected direction, all atomic columns are

mixed with S. Therefore, the average atomic number for Cu/S is 22.5, 21 for the Fe/S mixed column, and 15 for Si/S columns. The atomic number difference between Cu/S and Fe/S is 1.5, which is too small to have an intensity difference. Therefore, these columns should have similar bright intensities. However, Si/S should be easily identifiable with weak intensity. Therefore, the rows of bright spots with the same intensity represent the atomic Cu/S columns, and the neighboring rows with alternating weak and strong spots correspond to the rows of Si/S and Fe/S atoms. A HAADF-STEM image was also collected along the [100] direction; it shows alternating bright and dim spots, indicating the ordering of Fe/Si and Cu, similar to that observed for the Cu_2MnSiS_4 crystal.

However, for some crystals, the electron diffraction indicates the absence of (010) reflection, and the HAADF-STEM image shows rows of spots with the same intensity, indicating the disorder of Cu with Fe/Si in the crystal structure (Figure S2).
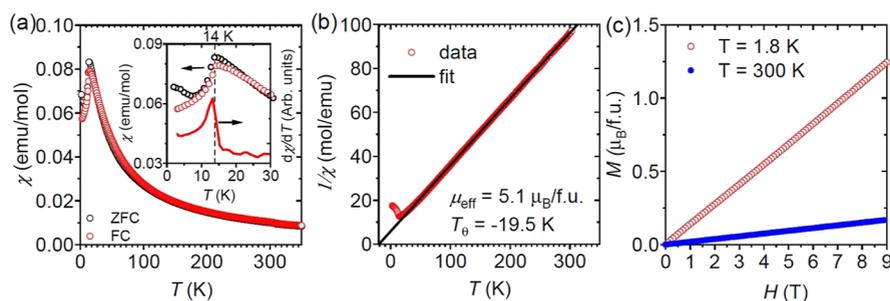
Figure 6. (a) Temperature-dependent ZFC−FC magnetic susceptibility at 0.1 T. Inset depicts the susceptibility data below 30 K (left axis) and the temperature derivative of the magnetic susceptibility (right axis), highlighting the kink that represents the magnetic phase transition. The dashed line is the guide to the eye for 14 K. (b) Inverse magnetic susceptibility fit with the Curie−Weiss law, and (c) field-dependent magnetization of polycrystalline Cu_2FeSiS_4.

The possible disorder structure might be similar to that of $Cu_2CoGeSe_4$ with the $F222$ space group, in which Cu, Co, and Ge are disordered and occupy the $4a$ $(0, 0, 0)$ site in the crystal structure.[12] Another disordered crystal structure in the CTMS-related system is $Cu_2NiSnSe_4$ ($F\bar{4}3m$), with Cu, Ni, and Sn atoms also occupying $4a$ $(0, 0, 0)$, the same as the above site.[12] The XRPD of this possible disordered structure is different from the polar crystal structure of $Pmn2_1$, and the corresponding peaks are not present in our patterns, indicating that the amount of such a disordered sample is too small to be detected in our X-ray or neutron powder patterns. The magnetic and optical properties should not be measurably affected by these small inclusions.

Chemical Analysis. Semiquantitative SEM−EDX measurements were performed on Cu_2TSiS_4 (T = Mn and Fe) crystals. The EDX maps of the selected area ($\sim$100 μm $\times$ 100 μm) of the surface of the crystal indicate that the Cu, Mn, Si, and S elements are homogeneously distributed (Figure S3). The calculated molar ratio of Cu/Mn:Si/S is 1.93:1:1.08:4.29, which is close to the expected 2:1:1:4 ratio. Similar homogeneous distribution of Cu, Fe, Si, and S elements is also observed in the Cu_2FeSiS_4 crystal with the obtained molar ratio of Cu/Mn/Fe/S = 1.95:1:1.02:4.08 (Figure S4).

Magnetic Properties. ZFC-FC magnetic measurements on polycrystalline Cu_2MnSiS_4 and Cu_2FeSiS_4 samples show AFM ordering at 8 (Figure 5a) and 14 K (Figure 6a), respectively, which are consistent with the reported values (8 and 15 K), as shown in Table 3.[16] The Curie−Weiss ($\chi = C/(T − T_\theta)$) fitting of the inverse magnetic susceptibility gives a negative Weiss constant $T_\theta = −12.5$ (Figure 5b) and −19.5 K (Figure 6b) for Cu_2MnSiS_4 and Cu_2FeSiS_4, respectively, indicating AFM coupling between Mn/Fe moments. The $\mu_{eff}(Mn^{2+})$ obtained from the Curie−Weiss fitting of Cu_2MnSiS_4 data is 5.7 μ_B, which is also close to the theoretical value of $\mu_{eff}(Mn^{2+}) = 5.92$ μ_B and the reported values ($\mu_{eff} = 5.9$ μ_B, $T_\theta = −17$ K) for Cu_2MnSiS_4.[33] The $\mu_{eff}(Fe)$ obtained from the Curie−Weiss fitting of Cu_2FeSiS_4 data is 5.13 μ_B, which is close to the theoretical value of $\mu_{eff}(Fe^{2+}) = 4.9$ μ_B. The linear behavior of field-dependent magnetization (Figures 5c and 6c) at 1.8 K also confirms the AFM ordering in both compounds. The AFM ordering with low T_N has also been observed in other Cu_2TMS_4 (T = Mn, Fe, Co, and Ni; M = Si, Ge, and Sn), as shown in Table 3.

Neutron Diffraction. Among the reported compounds of the CTMS family, only Cu_2MnGeS_4, Cu_2MnSnS_4, and Cu_2FeGeS_4 have had their magnetic structures investigated (Table 3).[13,15] To determine the magnetic structures of

Table 3. Summary of Magnetic Properties of Cu_2TMS_4 (T = Mn, Fe, Co, and Ni; M = Si, Ge, and Sn)

Compound	space group	T_N, K	k vector	magnetic space group	refs
Cu_2MnSiS_4	$Pmn2_1$	8, 8[a]	(1/2,0,1/2)	P_ac[a]	16, 33
Cu_2FeSiS_4	$Pmn2_1$	15, 14[a]	(1/2,1/2,1/2)[a]	C_ac[a]	12, 16
Cu_2CoSiS_4	$I\bar{4}2m$				34
Cu_2NiSiS_4					
Cu_2MnGeS_4	$Pmn2_1$	8.3, 9	(1/2,0,1/2)	P_ac	13, 16, 20, 35, 36
Cu_2FeGeS_4	$I\bar{4}2m$	12, 17	(1/2,0,1/2)		12, 15, 16, 33
Cu_2CoGeS_4	$I\bar{4}2m$	25			33, 34
Cu_2NiGeS_4	$I\bar{4}2m$, $I\bar{4}$	36			33, 37, 38
Cu_2MnSnS_4	$I\bar{4}2m$	8.8, 10	(1/2,0,1/2)	P_a2_1	13, 14, 16, 20, 39
Cu_2FeSnS_4 (β)	$I\bar{4}2m$	6.1, 7, 8			9, 40−42
Cu_2FeSnS_4 (α)	$P\bar{4}$	38			11, 43
Cu_2CoSnS_4	$I\bar{4}2m$				34
Cu_2NiSnS_4	$F\bar{4}3m$				12

[a]This work.

Cu_2MnSiS_4 and Cu_2FeSiS_4, NPD measurements were performed between 90−2 K and 100−2 K, respectively. Selected NPD patterns are shown in Figure 7. For the Cu_2MnSiS_4 sample, the pattern remains the same as the temperature decreases from 90 to 7.5 K, but new magnetic reflections show up below approximately 7.5 K, and their intensities increase as the temperature decreases. The observation of magnetic reflections at 7 K confirms the AFM transition determined by the magnetic measurements (Figure 5a). By comparison of the NPD patterns of 90 and 2 K (Figure S5), the obvious six magnetic reflections appearing at a lower temperature can be identified at 9.3, 5.3, 4.65, 3.97, 3.38, and 3.04 Å. For the Cu_2FeSiS_4 sample, new magnetic reflections appear below 14 K, which also supports the AFM ordering observed in the magnetic data (Figure 6a). The intensity of magnetic reflections increases as the temperature decreases to 2 K (Figure 7b). There are eight obvious peaks attributed to the magnetic structure being located at 7.6, 4.31, 3.89, 3.77, 3.12, 2.89, 2.54, and 2.47 Å (Figures 7b and S5).

In the NPD data of Cu_2MnSiS_4 collected at 2 K, the observed magnetic peaks can be indexed using the magnetic propagation vector $k = (1/2,0,1/2)$, with the most intense peak $(1/2,0,1/2)$ located at 9.3 Å. The nuclear peaks observed at 2
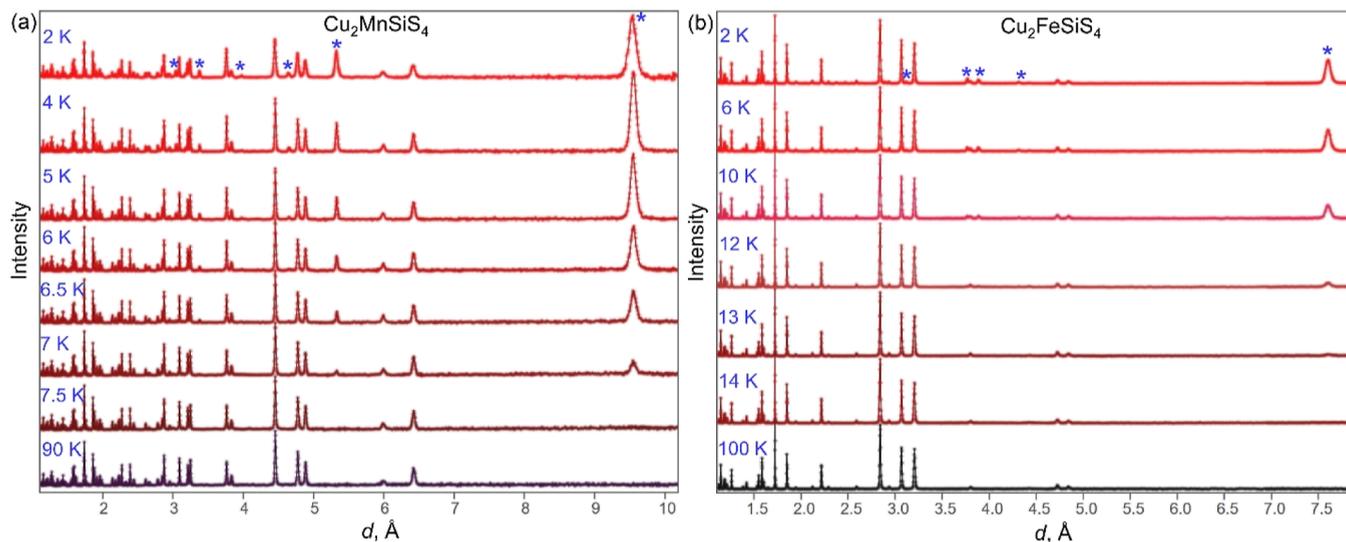
Figure 7. (a) Selected NPD patterns of Cu_2MnSiS_4 between 90 and 2 K and (b) Cu_2FeSiS_4 between 100 and 2 K. Magnetic peaks are marked with a star (*) symbol. For clarity purposes, only a few of the strongest peaks are marked.
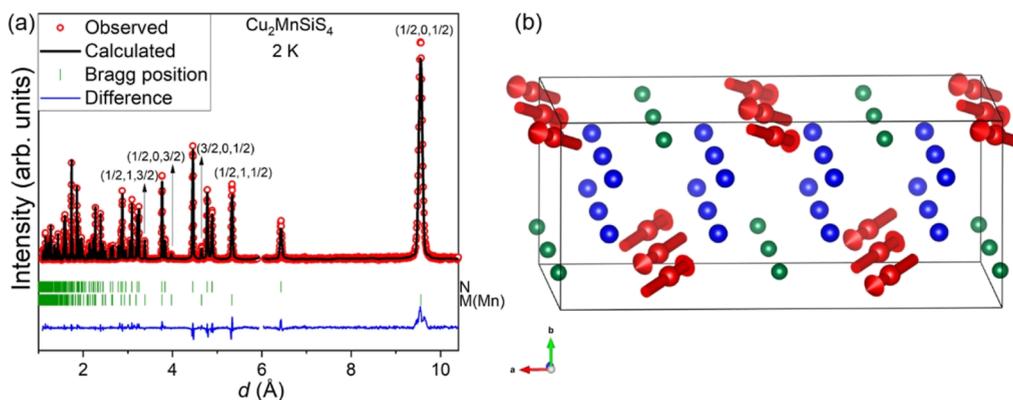
Figure 8. (a) Rietveld refinement of Cu_2MnSiS_4 (space group $Pmn2_1$) using NPD data (2 K) with observed data (red), the calculated pattern (black), difference between the observed and calculated patterns (blue), and Bragg peak positions of major nuclear and magnetic reflections (green). (b) Magnetic structure of Cu_2MnSiS_4 (color code: Cu = blue, Mn = red, and Si = green; S atoms are omitted for clarity).
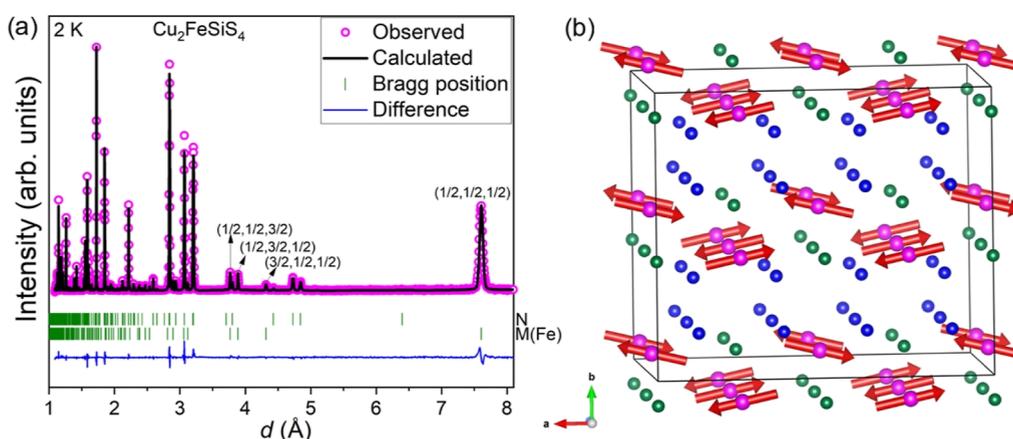
Figure 9. (a) Rietveld refinement of Cu_2FeSiS_4 (space group $Pmn2_1$) using NPD (2 K) data, with observed data (red), the calculated pattern (black), the difference between the observed and calculated patterns (blue), and Bragg peak positions of nuclear and magnetic reflections (green). (b) Magnetic structure of Cu_2FeSiS_4 (color code: Cu = blue, Fe = magenta, and Si = green, and S atoms are omitted for clarity).

K can be fit well with the same nuclear structure model used for the 90 K data set (Figure 8a). The refined unit cell parameters and atomic positions show a very small difference between the two temperatures (Table 1). The only magnetic

ions in the unit cell are Mn^{2+} ions, occupying only one Wyckoff position, $2a$. The best-fitting magnetic structure model involves an alignment of Mn magnetic moments along the MnS_4 tetrahedral edge, with the Mn pair inside the chemical unit

cell having the m_a and m_c components parallel but the m_b components antiparallel to each other. The moments are alternating their directions along the a and c directions, resulting in an overall antiferromagnetic structure. The determined magnetic structure is shown in Figure 8b, with the magnetic unit cell doubled in a and c directions as compared to the nuclear structure. This magnetic structure adopts the magnetic space group P_ac (#7.27).[23] The refined magnetic components of Mn at 2 K are m_a = 2.25(5) μ_B, m_b = 1.0(1) μ_B, and m_c = −3.18(5) μ_B, which yield a total magnetic moment m_{Mn} of 4.1(1) μ_B. The canting angle away from the ac plane is about 14°. Other refined parameters of the magnetic structure are given in Table S4.

This magnetic propagation vector of Cu_2MnSiS_4 is the same as that of isostructural Cu_2MnGeS_4 and stannite Cu_2MnSnS_4 (space group $I\overline{4}2m$),[13,14] and the refined magnetic moment (4.1 μ_B) for Cu_2MnSiS_4 is just slightly smaller than that obtained for other compounds: ~4.3 μ_B (Cu_2MnGeS_4) and ~4.28 μ_B (Cu_2MnSnS_4).[13,14] The isostructural Cu_2MnGeS_4 has been reported to be ordered with the same magnetic space group symmetry P_ac, but the moments are rotated from the c direction toward the b axis ($m_a \approx$ 2.6 μ_B, m_b = 3.3 μ_B, and m_c = 0.9 μ_B).[13] Cu_2MnSnS_4 exhibits a collinear AFM magnetic structure (magnetic space group P_a2_1) with k = (1/2,0,1/2), in which the magnetic moments are constrained by symmetry to lie in the ac plane (m_b = 0 μ_B). Nevertheless, the moments are still mainly oriented toward the edge of the MnS_4 tetrahedra, with a small deviation of 11 ± 5° away from the crystallographic c axis.[14]

The magnetic peaks that appear in the low-temperature (T < 14 K) NPD data of Cu_2FeSiS_4 can be indexed by the wave vector k = (1/2,1/2,1/2). The nuclear contribution to the NPD data collected at 2 K can be fit well using the same structural model as that used for the refinement using the data obtained at 100 K (Figure 9a). The refined unit cell parameter and atomic positions almost remained the same. The determined magnetic structure model that accounts well for all magnetic intensities is displayed in Figure 9b. Similar to Cu_2MnSiS_4, the two equivalent sites of the nuclear cell [(Fe^{2+} located at (0, 0.155, 0.509) and (0.5, 0.845, 0.009)] have parallel m_a and m_c components but antiparallel m_b. The magnetic moments alternate their directions along all three crystallographic directions, leading to a magnetic unit cell eight times larger than the nuclear lattice. The corresponding magnetic space group is C_ac (#9.41). The refined magnetic components of Fe at 2 K are m_a = 2.85(3) μ_B, m_b = 0.7(1) μ_B, and m_c = 0.5(1) μ_B, which yields a total magnetic moment of 2.9(1) μ_B. The spin axis is oriented at about 14° from the ac plane, which is very similar to the canting determined for the Mn congener. Other refined parameters of the magnetic structure are given in Table S5.

The determined magnetic structures for both investigated compounds can be viewed as consisting of chains of collinear spins that are arranged antiferromagnetically along the c direction. The magnetic moments of adjacent chains are canted with respect to each other around the b axis. While in the Mn compound, the direction of the spins only alternates inside the chain (c axis) and along the a axis; in the Cu_2FeSiS_4 compound, the Fe spins are alternating their orientation in all crystallographic directions. A propagation vector k = (1/2,0,1/2) has been observed for all studied Mn systems [Cu_2MnSiS_4, Cu_2MnGeS_4, Cu_2MnSnS_4 (space group $I\overline{4}2m$)] and also for Cu_2FeGeS_4 (space group $I\overline{4}2m$).[13–15] In the latter, four

distinct magnetic structure models compatible with the propagation vector k = (1/2,0,1/2) have been discussed, but the final model has not been determined.[15] The magnetic structure of the other related Fe-containing sulfide, Cu_2FeSnS_4, has not been reported. Considering selenides and tellurides as well, Cu_2FeGeS_4 is the first example with a k = (1/2,1/2,1/2) magnetic order in the quaternary Cu_2FeMX_4 (M = Si, Ge, and Sn; X = S, Se, and Te) chalcogenide family. The propagation vector k = (1/2,1/2,1/2) and a similar magnetic moment of Fe (2.82 μ_B) have also been observed in the related Li_2FeGeS_4, a polar (space group Pn) antiferromagnet ($T_N \sim$ 6 K) with collinear magnetic Fe spins along the b axis, which is different from the incommensurate [k = (0,0,0.546)] collinear magnetic structure in the polar (space group Pn) antiferromagnet ($T_N \sim$ 4 K) Li_2FeGeS_4.[44]

Attenuated Total Reflectance−Fourier Transform Infrared Spectroscopy. ATR−FT-IR spectroscopy was used to assess the windows of optical clarity for Cu_2TSiS_4 (T = Mn and Fe). Accurate and extreme transparency necessary for NLO devices should be determined using high-quality single-crystal specimens, but ATR−FT-IR of micro-crystalline samples provides a general idea of the transparency. As expected for sulfides, the IR transparency is very high, with both compounds exhibiting values above 80% transparency throughout the entire measured range of 2.5 to 25 μm (Figure S6).

Second-Order NLO Property Measurements. Using an incident wavelength of λ = 1800 nm, the SHG dependence on the particle size was investigated for the title compounds and compared to that of the NLO reference materials. The AGS reference exhibits a clear phase-matching (PM) trend, as indicated by increasing SHG counts with increasing particle size. This result is consistent with the known PM onset, which is indeed λ = 1800 nm for AGS. On the other hand, the SHG response of the title compounds does not increase with increasing particle size, signifying that they are non-phase-matching (NPM) at this wavelength. Normally, broadband NLO studies would be performed to search for a possible PM onset, as most related compounds that have been studied are PM at some longer wavelengths; however, this was not possible for the title compounds. The Cu_2TSiS_4 (T = Mn and Fe) samples did not exhibit enough SHG counts in the mid-IR, λ > 2400 nm to be detected with an InGaAs detector, and they did not have a measurable response for λ = 1064 nm either. Therefore, the SHG coefficients of the title compounds were assessed by comparing them with the SHG counts from AGSe, which is also NPM at λ = 1800 nm.

It should be noted that because the title compounds did not exhibit a measurable SHG response at λ = 1064 nm, the laser-induced damage thresholds (LIDTs), which are almost always reported for λ = 1064 nm, could not be assessed. However, given the relatively narrow optical band gaps of the title compounds, outstanding LIDTs are not anticipated.

The second-order NLO susceptibility of each sample, $\chi_S^{(2)}$, was calculated by comparing it with that of AGSe using the Kurtz powder method for the NPM case;[45] where I_S^{SHG} and I_R^{SHG} are the experimentally measured SHG counts from the test sample and the reference, respectively.

$$\chi_S^{(2)} = \chi_R^{(2)} \frac{l_R}{l_S} \left(\frac{I_S^{SHG}}{I_R^{SHG}} \right)^{1/2}$$

(1)
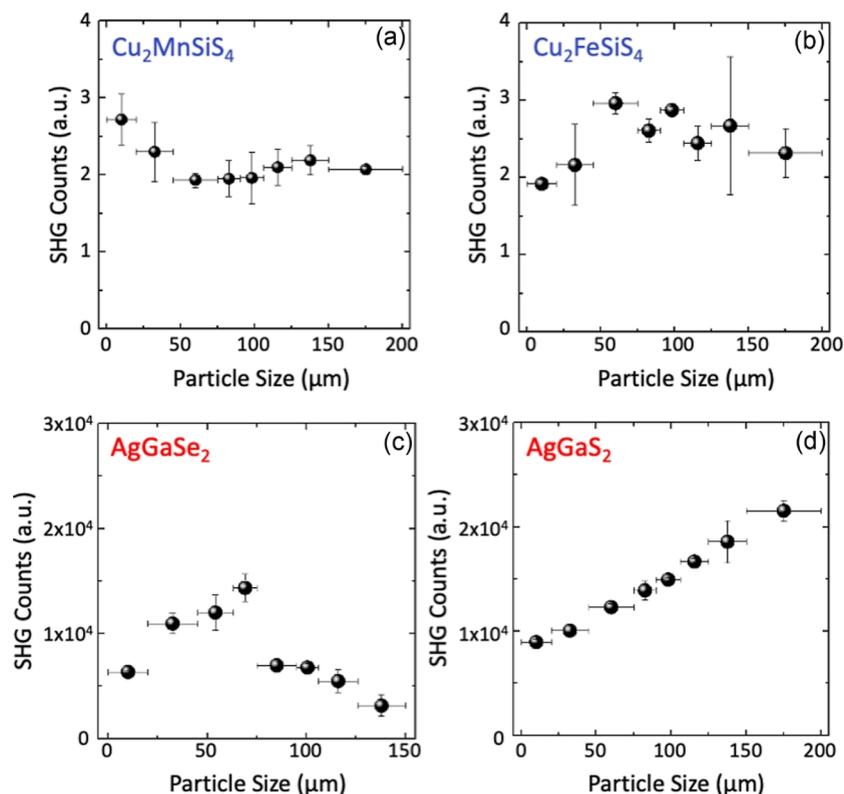
Figure 10. Particle size dependence of the SHG response for (a) Cu_2MnSiS_4 and (b) Cu_2FeSiS_4 compared to that of the (c) AGSe and (d) AGS reference materials. At this incident wavelength, $\lambda = 1800$ nm (i.e., $\lambda_{SHG} = 900$ nm), only the AGS is phase matchable.

In eq 1, l_S and l_R are the experimentally measured coherence lengths that correspond to the maximum SHG counts in Figure 10. Using $\chi_R^{(2)} \sim 66$ pm/V for AGSe,[46] our calculation yields $\chi_S^{(2)}$ $(Cu_2MnSiS_4) \sim 6.27 \pm 0.07$ pm/V and $\chi_S^{(2)}$ $(Cu_2FeSiS_4) \sim 1.09 \pm 0.03$ pm/V, respectively. Although both compounds exhibit rather similar SHG counts, the difference in $\chi_S^{(2)}$ arises from the difference in the coherence lengths. While both title compounds definitely yield a finite SHG response, the SHG intensities are quite weak compared with AGSe and AGS $(\chi_R^{(2)} \sim 36$ pm/V) (b),[47] which are benchmark IR-NLO materials, and the resulting $\chi_S^{(2)}$ values are expectedly modest.

To put things into perspective, one can consider these results for the title compounds in the context of other quaternary chalcogenides with the same or similar crystal structures. Although the nonpolar $Cu_2ZnGeSe_4$ (space group $I\bar{4}$) with the kesterite structure has a similar band gap (1.38 eV) to Cu_2MnSiS_4 (theoretical $E_g^{direct} = 1.73$ eV as shown in Figure 12), it has a much better SHG performance with $\chi_S^{(2)} \sim 43$ pm/V.[48] On the other hand, the polar $Cu_4ZnGe_2Se_7$ (space group $C2$), which has a more complex superstructure of zinc blend and a narrower optical band gap (0.91 eV), only exhibited a very weak SHG response, such that the $\chi_S^{(2)}$ value was not determined.[48] The polar Li_2MnGeS_4 (space group $Pna2_1$) with a different superstructure of the W structure demonstrates a similar SHG efficiency as Cu_2MnSiS_4, $\chi_S^{(2)} \sim 6.6$ pm/V, although the optical band gap of the former is much wider (3.07 eV).[49] Some other compounds with the same WSt structure as the title compounds, such as Cu_2MnGeS_4 and Li_2CdGeS_4, not only have much stronger SHG responses with $\chi_S^{(2)} \sim 16.9$ pm/V and $\chi_S^{(2)} \sim 22.5$ pm/V but also possess considerably larger optical band gaps of 2.21 and 3.15 eV,
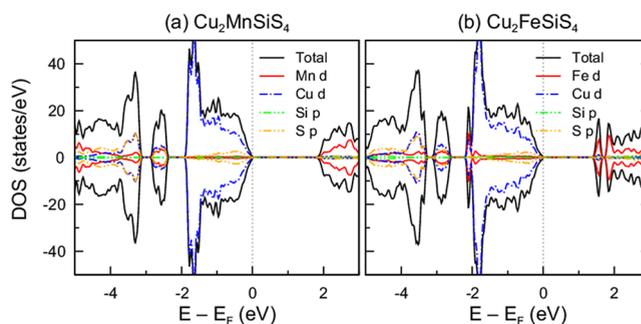
Figure 11. Total and partial densities of states (DOS) of (a) Cu_2MnSiS_4 and (b) Cu_2FeSiS_4 with collinear AFM structures. The positive and negative values in DOS correspond to spin-up and -down configurations, respectively.

respectively.[1,18,19] In a nutshell, the performance of the title compounds lies in the same realm as related materials, which vary widely in their SHG responses and optical band gap energies.

Electronic Structure Calculations. DFT calculations were carried out to investigate the electronic structures of Cu_2MSiS_4 (M = Mn and Fe). From the NPD experiments, these systems show canted AFM ordering. In the spin-polarized DFT calculations, however, collinear AFM structures were used instead for both systems for simplicity. This simplification might change the details of the electronic structure but does not alter the general conclusion of this study.

DFT calculations were performed with on-site Coulomb repulsion parameters $U_{eff} = 4$ and 5 eV chosen for Cu_2MnSiS_4 and Cu_2FeSiS_4, respectively. Those values are comparable to
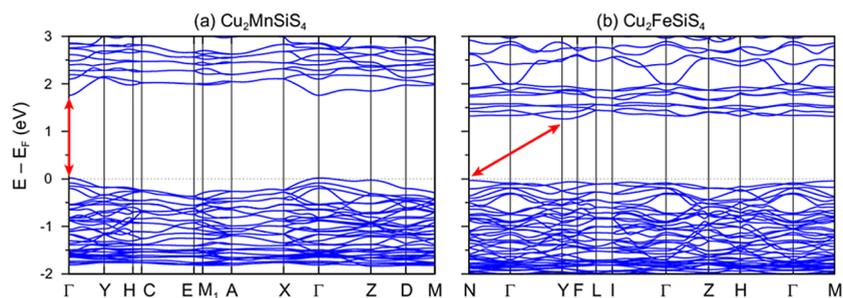
Figure 12. Band dispersions of (a) Cu_2MnSiS_4 and (b) Cu_2FeSiS_4 (b) with collinear AFM structures.

those used in previous DFT studies on similar compounds.[50,51] The DOS for both systems with collinear AFM structures are presented in Figure 11. The DFT calculations show that both systems are semiconductors with band gaps >1 eV. The band gap is formed between the top of the valence band with mostly Cu d character and the bottom of the conduction band with mostly Mn (Fe) d character in the case of Cu_2MnSiS_4 (Cu_2FeSiS_4). The character of dominating Cu d orbitals near valence band maximum (VBM) is also observed in Cu_2MGeS_4 (T = Mn and Ni) and Cu_2TSnS_4 (M = Mn, Fe, and Ni),[50,52−54] which is different from the character of hybridization of Cu d and S p found in Cu_2CoMS_4 (M = Ge, Sn).[55,56] The feature of T d orbitals near the conduction band minimum (CBM) of Cu_2TSiS_4 (T = Mn and Fe) is similar to that of Cu_2NiMS_4 (M = Ge and Sn),[38,53,54] and Cu_2CoGeS_4,[55] which is different from the hybridization of Mn d, Ge s, and S p in Cu_2MnGeS_4,[52] Sn s and S p in Cu_2TSnS_4 (M = Mn and Fe),[54] and Co d and S p in Cu_2CoSnS_4.[56]

The DFT calculations indicate that ordered magnetic moments are only realized in Mn (Fe) sites for Cu_2MnSiS_4 (Cu_2FeSiS_4). The size of the ordered magnetic moment is 4.55 μ_B/Mn and 4.35 μ_B/Fe for Cu_2MnSiS_4 and Cu_2FeSiS_4, respectively. Magnetic exchange interaction was also estimated within the DFT framework by computing an energy difference between the ferromagnetic (FM) and collinear AFM magnetic ordering phases, that is, $E_{FM} - E_{AFM}$. The magnitudes of the computed magnetic exchange interactions are 3.38 meV per Mn and 4.39 meV per Fe for Cu_2MnSiS_4 and Cu_2FeSiS_4, respectively.

Band structure calculations indicate that Cu_2MnSiS_4 is a semiconductor with a direct band gap (E_g^{direct} = 1.73 eV) located at Γ, while Cu_2FeSiS_4 has an indirect band gap ($E_g^{indirect}$ = 1.52 eV) formed from N (VBM) to Y (CBM) (Figure 12). The calculated band gaps are in a reasonable range compared to those calculated for the previously reported CTMS and related compounds: Ag_2FeSiS_4 (E_g^{direct} = 1.99 eV),[57] Cu_2MnGeS_4 (E_g^{direct} = 1.72 eV),[52] Cu_2FeGeS_4 (E_g^{direct} = 1.8 eV),[58] Cu_2CoGeS_4 (E_g^{direct} = 0.81 eV),[55] Cu_2NiGeS_4 (E_g^{direct} = 1.76, 1.78 eV),[53] Cu_2MnSnS_4 (E_g^{direct} = 1.4, 1.52 eV),[54,59] Cu_2FeSnS_4 (E_g^{direct} = 1.7 eV),[54] Cu_2CoSnS_4 (E_g^{direct} = 1.2 eV),[56] and Cu_2NiSnS_4 (E_g^{direct} = 1.29 eV).[54] The indirect band gap is already reported in Ag_2MnSnS_4 ($E_g^{indirect}$ = 2.00 eV) and Li_2FeSnS_4 ($E_g^{indirect}$ = 1.42 eV) based on optical measurements.[44,60]

CONCLUSIONS

Both polycrystalline and single-crystal Cu_2TSiS_4 (T = Mn and Fe) have been successfully prepared and adopt the same WSt polar crystal structure supported by NPD, X-ray powder and single-crystal diffraction, TEM, and SHG measurements. The

polar crystal structure also remains below 100 K based on temperature-dependent NPD experiments. Although Cu_2TSiS_4 (T = Mn and Fe) adopt the same crystal structure and show similar AFM behavior at low temperatures, their magnetic structures are distinct, with different magnetic propagation vectors. Interestingly, both magnetic Mn and Fe spins are canted away from the ac plane by about the same degree. Cu_2TSiS_4 (T = Mn and Fe) also show SHG responses, which fall in the same realm as related compounds, but both compounds are not PM in the region where they perform best. DFT calculations suggest the direct band gap for Cu_2MnSiS_4 and the indirect band gap for Cu_2FeSiS_4. As members of CTMS, Cu_2TSiS_4 (T = Mn and Fe) compounds are polar magnetic semiconductors with NLO responses as well, which is rare in this series. The detailed study of the polar crystal structure, magnetic structure, electronic structure, optical transparency in the IR region, and NLO responses will benefit the investigation of the large family of $AB^{II}M^{IV}X_4$ (A = alkali metals, Cu, and Ag; B = alkaline earth metals, transitional metals, Pb, and Eu; M = Si, Ge, and Sn; X = O, S, Se, and Te) compounds as multifunctional magnetic semiconductors with potential applications in photovoltaic, NLO, ferroelectric, magnetoelectric, and multiferroic areas.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c03754.

> X-ray single-crystal data collection and structure refinement parameters of Cu_2TSiS_4 (T = Mn and Fe); XRPD patterns of Cu_2TSiS_4 (T = Mn and Fe); electron diffraction of Cu_2FeSiS_4; EDX elemental maps and SEM image of Cu_2TSiS_4 (T = Mn and Fe) single crystals; NPD patterns of Cu_2MnSiS_4 at 90 and 2 K and Cu_2FeSiS_4 at 100 and 2 K; and FT-IR−ATR data plotted as percent transmittance for Cu_2TSiS_4 (T = Mn and Fe) (PDF)

Accession Codes

CCDC 2211728 and 2211730 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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