Polymorphism and Second Harmonic Generation in a Novel Diamond-like Semiconductor: $\text{Li}_2\text{MnSnS}_4$

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Abstract:

High-temperature, solid-state synthesis in the $\text{Li}_2\text{MnSnS}_4$ system led to the discovery of two new polymorphic compounds that were analyzed using single crystal X-ray diffraction. The α -polymorph crystallizes in $Pna2_1$ with the lithium cobalt (II) silicate, $\text{Li}_2\text{CoSiO}_4$, structure type, where $Z=4$, $R1=0.0349$ and $wR2=0.0514$ for all data. The β -polymorph possesses the wurtz-kesterite structure type, crystallizing in Pn with $Z=2$, $R1=0.0423$, and $wR2=0.0901$ for all data. Rietveld refinement of synchrotron X-ray powder diffraction was utilized to quantify the phase fractions of the polymorphs in the reaction products. The α/β - $\text{Li}_2\text{MnSnS}_4$ mixture exhibits an absorption edge of ~ 2.6 - 3.0 eV, a wide region of optical transparency in the mid- to far-IR, and moderate SHG activity over the fundamental range of 1.1 - 2.1 μm . Calculations using density functional theory indicate that the ground state energies and electronic structures for α - and β - $\text{Li}_2\text{MnSnS}_4$, as well as the hypothetical polymorph, γ - $\text{Li}_2\text{MnSnS}_4$ with the wurtz-stannite structure type, are highly similar.

Keywords: sulfide, polymorphism, stannite, kesterite, SHG

1. Introduction

Diamond-like semiconductors possess crystal structures that can be derived from that of diamond, either the cubic or hexagonal form [1,2]. The first derivation from diamond produces binary materials, such as ZnS. The familiar zincblende and wurtzite structures of ZnS are derived from the cubic and hexagonal diamond structures, respectively. Surprisingly, there are over 190 polymorphs of ZnS. The structures can be thought of as the assemblage of layers of cubic and hexagonal closest packed anions with the cations occupying half of the tetrahedral holes [3]. The number and thickness of the layers are different for each polymorph. For example, zincblende is a face-centered cubic lattice of repeating layers, ABCABC (c_3), and wurtzite is a hexagonal closest packed lattice of repeating layers, ABAB (h_2). A ZnS polymorph known as 28T, in the Ramsdell notation [4], has two repeating motifs: 1) a hexagonal layer (h) and eight cubic layers (c), are repeated twice, and 2) a hexagonal layer and four cubic layers are repeated twice. Therefore, the structure can be expressed as $((hc_8)_2(hc_4)_2)$ [3].

When diamond-like compounds contain more than one cation, nature has the opportunity not only to choose the packing of the anions, but also to designate the cation-ordering pattern within the anion array resulting in multiple structure types, as illustrated in Figure 1. In the case of ternary diamond-like semiconductors there are several structures that exist, such as chalcopyrite [5,6] and famatinite [7,8], that differ in cation ordering patterns but have the same cubic closest packing of anions, being derived from the cubic zincblende structure [9].

Figure 1. Selected, ordered binary, ternary, and quaternary hexagonally derived diamond-like semiconductors. The space group of each structure type is dictated by the cation arrangement within the tetrahedral holes of the hexagonal closest-packed arrays of anions.

In the case of quaternary materials, there are six structure types that have been commonly reported, three of which are derived from the cubic diamond structure, stannite (*I-42m*) [10,11], kesterite (*I-4*) [11] and disordered kesterite (*I-42m*) [12] and three that are derived from hexagonal diamond, lithium cobalt (II) silicate, $\text{Li}_2\text{CoSiO}_4$ (*Pna2₁*) [13,14], wurtz-stannite (*Pmn2₁*) [9], and wurtz-kesterite (*Pn*) [9]. Using twenty-four $\text{I}_2\text{-II-IV-VI}_4$ compositions, Chen et al. calculated the relative stabilities of stannite, kesterite, wurtz-stannite, and wurtz-kesterite structures [15]. The *Pna2₁* structure, which has a larger volume unit cell, was not considered in Chen's study. Their calculations show that in some instances there is little energy difference between the calculated ground state for a cubic-derived structure and a hexagonal-derived structure. For example, the calculated energy difference between kesterite and wurtz-kesterite structures in $\text{Ag}_2\text{ZnGeS}_4$ is -0.1 meV/atom. In other cases, there are only slight variations in the calculated ground state energies for different structure types of the same kind of closest packing. For example, the calculated ground state energy difference between wurtz-kesterite (*Pn*) and wurtz-stannite (*Pmn2₁*) structures of $\text{Cu}_2\text{ZnSnS}_4$ is -1.2 meV/atom. In the case of the cadmium analog, $\text{Cu}_2\text{CdSnS}_4$, the wurtz-stannite (*Pmn2₁*) structure is favored by 1.2 meV/atom [15].

Recently, it has been shown that more than one structure can be stabilized for a given quaternary composition. For example, the stannite (*I-42m*) structure and the wurtz-stannite (*Pmn2₁*) structure were determined for $\text{Cu}_2\text{CdGeSe}_4$ [16] using X-ray powder diffraction (XRPD) and single crystal X-ray diffraction, respectively [9,17]. Stannite (*I-42m*) has the lowest ground state energy for $\text{Cu}_2\text{CdGeSe}_4$ and the wurtz-stannite (*Pmn2₁*) structure exhibits the second lowest energy according to the calculations put forth by Chen et al. [15]. In another example, $\text{Cu}_2\text{ZnSiS}_4$ crystallizes in both the wurtz-stannite (*Pmn2₁*) [18,19] and wurtz-kesterite (*Pn*) structures, as observed using single crystal X-ray diffraction and synchrotron X-ray powder diffraction data (SXRPD), respectively [20]. The SXRPD data also confirms the presence of both polymorphs in a single sample. For this compound, Chen et al. predict the kesterite (*I-4*) structure to be the most stable and the wurtz-kesterite (*Pn*) structure as the next most stable, with a ground state energy difference of only 0.3 meV/atom. The third most stable structure, wurtz-stannite (*Pmn2₁*), has a calculated ground state energy that differs from that of kesterite (*I-4*) by 2.4 meV/atom. Several authors have reported the structure of $\text{Ag}_2\text{CdGeS}_4$ as wurtz-stannite (*Pmn2₁*) type [9-23], while others have reported the lithium cobalt (II) silicate (*Pna2₁*) structure [24] that was not considered in Chen's study. For this compound, Chen et al. predicted the wurtz-kesterite (*Pn*) structure as the most stable, with ground state energy 2.8 meV/atom lower than that of wurtz-stannite (*Pmn2₁*). Discrepancies between the predicted and observed structures may be a result of the athermal conditions under which the calculations are performed or the presence of defects and/or impurities in the real samples that can alter the ground state energies.

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS), a highly promising candidate for next-generation solar cells, exhibits the kesterite (*I-4*) structure when the bulk material is formed under conditions of slow cooling, as predicted by Chen et al. [15]; however, reactions that are rapidly cooled or quenched from high temperature exhibit a disordered kesterite structure that crystallizes in the space group *I-42m* [12,25]. More recently, local structure methods have illustrated a more complex picture for $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles, where the clustering of Cu_{Zn} and Zn_{Cu} antisites across multiple unit cells is proposed [26]. The formation of different structures in this system has been attributed to the low formation energy of the $\text{Cu}_{\text{Zn}} + \text{Zn}_{\text{Cu}}$ antisite defect pair [27]. Moreover, certain synthetic conditions have even provided access to $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles with a wurtzite structure, in which all three cations are disordered on one crystallographic site [28].

With the high probability of polymorphism in these diamond-like systems, great care should be taken in identifying the structure type(s) for a given composition. There can be difficulty or ambiguity in differentiating between structures types. For example, there exists a close resemblance in the calculated XRPD patterns for the different quaternary diamond-like structures that can make them difficult or impossible to distinguish using laboratory-grade XRPD. One cause for the likeness in diffraction patterns is the similar lattice parameters for some structure types, e.g., wurtz-stannite versus wurtz-kesterite [29]. Similarities in XRPD patterns also can arise when the X-ray scattering factors [30,31] for some atoms in the compound are nearly identical, such as isoelectronic Ag^+ and Cd^{2+} in $\text{Ag}_2\text{CdGeS}_4$ [24]. However, the use of high-intensity, high-resolution SXRPD or sophisticated methods such as X-ray resonant single crystal diffraction may result in a definitive assignment of structure type [12,24].

Structure type can have important influence on the physicochemical properties of a material, which is clearly illustrated in the different birefringence values of ZnS polymorphs. Large birefringence is one of the criteria for promising nonlinear optical (NLO) materials [32]. Cubic zincblende-type ZnS is optically isotropic and has a birefringence of zero. However, the wurtzite structure has a large birefringence value. The birefringence values for other ZnS polytypes fall between those of zincblende and wurtzite depending on how many cubic-closest packed and hexagonal-closest packed layers the polymorph contains [3].

High-temperature, solid-state reactions in the Li-Mn-Sn-S system yielded the new diamond-like $\text{Li}_2\text{MnSnS}_4$. Single crystal X-ray diffraction and high-resolution SXRPD show that $\text{Li}_2\text{MnSnS}_4$ exists as two polymorphs. Here we report the new compounds $\alpha\text{-Li}_2\text{MnSnS}_4$ and $\beta\text{-Li}_2\text{MnSnS}_4$, which crystallize in the lithium cobalt (II) silicate ($Pna2_1$) and wurtz-kesterite (Pn) structure types, respectively. The α - and β - $\text{Li}_2\text{MnSnS}_4$ mixture is analyzed using optical diffuse reflectance UV/Vis/NIR spectroscopy and attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy. Broadband second-order NLO property measurements were also conducted using the Kurtz-Perry powder method [33]. Electronic structure calculations for $\alpha\text{-Li}_2\text{MnSnS}_4$ and $\beta\text{-Li}_2\text{MnSnS}_4$, as well as a hypothetical $\gamma\text{-Li}_2\text{MnSnS}_4$ with the wurtz-stannite ($Pmn2_1$) structure type, indicate very little difference in the ground state energies between these polymorphs as well as similar features in the electronic band structure and density of states (DOS).

2. Experimental Section

2.1 Reagents.

All chemicals were used as obtained unless otherwise noted: lithium sulfide powder, ~200 mesh, 99.9%, Cerac; manganese chips, 0.8 – 3 mm, 99.99%, Cerac, were cleaned with hot 10% HNO_3 in methanol and then ground into powder in an argon-filled glovebox; tin powder, ~200 mesh, 99.99%, Cerac; sulfur powder, sublimed, 99.5%, Fisher Scientific.

2.2 Synthesis of $\alpha\text{-Li}_2\text{MnSnS}_4$ and $\beta\text{-Li}_2\text{MnSnS}_4$

$\text{Li}_2\text{MnSnS}_4$ single crystals were synthesized by weighing stoichiometric amounts of Li_2S , Mn, Sn and S in an argon-filled glove box. The reagents were combined and ground using an agate mortar and pestle. The starting materials were then transferred to a graphite crucible and placed into a 12 mm outer-diameter fused-silica tube. The tube was flame-sealed using an oxy-methane torch under a vacuum of $\sim 10^{-3}$

mbar. The sealed reaction tube was then placed into a programmable furnace and heated. The single crystals of α -Li₂MnSnS₄ and β -Li₂MnSnS₄ were selected from a reaction that was heated from room temperature to 800 °C over 11.3 h and held at that temperature for 30 h. The sample was allowed to cool to ambient temperature radiatively. The entire sample was rinsed with methanol in order to remove the Li₂S_x flux. Although the reaction was conducted stoichiometrically, excess Li₂S_x resulted due to the presence of unwanted phases. The product was examined under an optical microscope. The Li₂MnSnS₄ crystals are yellow-orange irregular polyhedra.

The polycrystalline sample of α -Li₂MnSnS₄ and β -Li₂MnSnS₄ with the highest phase purity that was analyzed by SXRPD was obtained by heating the reactants to 750 °C at a rate of 50 °C/h, holding the reaction at 750 °C for 144 h followed by slow cooling at a rate of 1 °C/h to 550 before cooling to room temperature radiatively.

2.3 Single Crystal X-ray Diffraction

Two single crystals were mounted onto glass fibers and analyzed using single crystal X-ray diffraction. Although both crystals were yellow/orange in color, the α -Li₂MnSnS₄ crystal was larger and deeper orange than the β -Li₂MnSnS₄ crystal.

A Bruker SMART Apex 2 CCD single crystal X-ray diffractometer using graphite-monochromatized molybdenum K α radiation (λ = 0.71073) was used to collect data at ambient temperature. Data were collected with a tube power of 50 kV and 30 mA for 35 s per frame. SAINT [34] was used to integrate the data and SADABS [35] was employed to perform the multi-scan absorption correction. XPREP was used for space group determination and to create files for SHELXTL [36]. In the case of α -Li₂MnSnS₄, two space groups were suggested based on systematic absences, *Pna*2₁ (No. 33) and *Pnma* (No. 62). For β -Li₂MnSnS₄, two space groups were also indicated based on the systematic absences, *Pn* (No. 7) and *P2/n* (No. 13). All diamond-like structures are noncentrosymmetric since all of the tetrahedra align along one crystallographic direction; therefore, space groups *Pna*2₁ and *Pn* were selected for α -Li₂MnSnS₄ and β -Li₂MnSnS₄, respectively. The SHELXTL-PC [36] software package was used to solve and refine the crystal structures. There are 8 crystallographically unique atoms in the α -Li₂MnSnS₄ and β -Li₂MnSnS₄ structures, where all atoms reside on general positions. Table 1 lists the crystallographic data and refinement details for both structures. Fractional atomic coordinates and equivalent isotropic displacement parameters are listed in Tables S1 and S2. Selected bond distances and angles are contained in Table 2.

Table 1: Summary of single crystal X-ray diffraction data and refinement details for α - and β -Li₂MnSnS₄.

Compound	α -Li ₂ MnSnS ₄	β -Li ₂ MnSnS ₄
Crystal System	Orthorhombic	Monoclinic
Space Group	<i>Pna2</i> ₁	<i>Pn</i>
Color	Yellow-orange	Yellow-orange
Unit Cell	a = 13.7036(3) Å b = 8.0023(2) Å c = 6.4155(2) Å	a = 6.4143(6) Å b = 6.8475(6) Å c = 8.0078(7) Å β = 89.980(6)°
Volume	703.53 (3) Å ³	351.72(5) Å ³
Z	4	2
Density	2981 kg/m ³	2981 kg/m ³
Crystal Size	0.080 × 0.047 × 0.043 mm	0.025 × 0.030 × 0.037 mm
Flack Parameter	0.04(3)	0.21(5)
Final R Indices (for I > 2 σ (I))	R1 = 0.0251, wR2 = 0.0484	R1 = 0.0362, wR2 = 0.0861
R Indices (all data)	R1 = 0.0349, wR2 = 0.0514	R1 = 0.0423, wR2 = 0.0901

Refinement of F^2 was made against all reflections. $R_1 = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$,

$wR_2 = \sqrt{(\sum [w(F_o^2 - F_c^2)^2]) / \sum [w(F_o^2)^2]}$, $w = 1/(\sigma^2(F_o^2) + (aF_o)^2 + bP)$, $P = [2F_c^2 + \text{Max}(F_o^2, 0)]/3$

Table 2: Selected bond distances and angles for α - and β -Li₂MnSnS₄ obtained from the single crystal X-ray diffraction.

α -Li ₂ MnSnS ₄ (<i>Pna2</i> ₁)				β -Li ₂ MnSnS ₄ (<i>Pn</i>)			
Bond Distances (Å)		Bond Angles (°)		Bond Distances (Å)		Bond Angles (°)	
Li(1)–S(1)	2.383(9)	S(1)–Li(1)–S(2)	114.2(3)	Li(1)–S(1)	2.39(3)	S(1)–Li(1)–S(2)	112.9(1)
Li(1)–S(2)	2.378(8)	S(1)–Li(1)–S(3)	113.8(4)	Li(1)–S(2)	2.36(3)	S(1)–Li(1)–S(3)	109.7(8)
Li(1)–S(3)	2.405(7)	S(1)–Li(1)–S(4)	108.0(4)	Li(1)–S(3)	2.58(3)	S(1)–Li(1)–S(4)	111.0(1)
Li(1)–S(4)	2.56(1)	S(2)–Li(1)–S(3)	109.9(3)	Li(1)–S(4)	2.49(1)	S(2)–Li(1)–S(3)	107.5(1)
		S(2)–Li(1)–S(4)	105.5(4)			S(2)–Li(1)–S(4)	109.3(8)
		S(3)–Li(1)–S(4)	104.7(3)			S(3)–Li(1)–S(4)	106.2(1)
Li(2)–S(1)	2.51(2)	S(1)–Li(2)–S(2)	107.5(6)	Li(2)–S(1)	2.49(4)	S(1)–Li(2)–S(2)	107(3)
Li(2)–S(2)	2.40(1)	S(1)–Li(2)–S(3)	105.2(6)	Li(2)–S(2)	2.53(7)	S(1)–Li(2)–S(3)	109(3)
Li(2)–S(3)	2.49(1)	S(1)–Li(2)–S(4)	107.2(6)	Li(2)–S(3)	2.35(9)	S(1)–Li(2)–S(4)	108(2)
Li(2)–S(4)	2.44(1)	S(2)–Li(2)–S(3)	110.7(6)	Li(2)–S(4)	2.41(6)	S(2)–Li(2)–S(3)	111(2)
		S(2)–Li(2)–S(4)	114.2(6)			S(2)–Li(2)–S(4)	109(3)
		S(3)–Li(2)–S(4)	111.4(6)			S(3)–Li(2)–S(4)	112(3)
Mn(1)–S(1)	2.445(3)	S(1)–Mn(1)–S(2)	110.9(2)	Mn(1)–S(1)	2.424(4)	S(1)–Mn(1)–S(2)	110.9(1)
Mn(1)–S(2)	2.425(3)	S(1)–Mn(1)–S(3)	110.3(1)	Mn(1)–S(2)	2.406(3)	S(1)–Mn(1)–S(3)	108.7(1)
Mn(1)–S(3)	2.433(6)	S(1)–Mn(1)–S(4)	110.3(2)	Mn(1)–S(3)	2.411(2)	S(1)–Mn(1)–S(4)	107.9(1)
Mn(1)–S(4)	2.443(3)	S(2)–Mn(1)–S(3)	109.1(2)	Mn(1)–S(4)	2.428(3)	S(2)–Mn(1)–S(3)	111.3(1)
		S(2)–Mn(1)–S(4)	107.9(1)			S(2)–Mn(1)–S(4)	110.6(1)
		S(3)–Mn(1)–S(4)	108.3(2)			S(3)–Mn(1)–S(4)	107.4(1)
Sn(1)–S(1)	2.383(2)	S(1)–Sn(1)–S(2)	110.38(8)	Sn(1)–S(1)	2.390(2)	S(1)–Sn(1)–S(2)	108.52(8)
Sn(1)–S(2)	2.391(3)	S(1)–Sn(1)–S(3)	110.78(8)	Sn(1)–S(2)	2.387(2)	S(1)–Sn(1)–S(3)	111.00(7)
Sn(1)–S(3)	2.385(2)	S(1)–Sn(1)–S(4)	107.68(7)	Sn(1)–S(3)	2.388(2)	S(1)–Sn(1)–S(4)	108.22(8)
Sn(1)–S(4)	2.391(2)	S(2)–Sn(1)–S(3)	108.76(8)	Sn(1)–S(4)	2.395(3)	S(2)–Sn(1)–S(3)	109.80(8)
		S(2)–Sn(1)–S(4)	108.39(8)			S(2)–Sn(1)–S(4)	110.21(8)
		S(3)–Sn(1)–S(4)	110.83(8)			S(3)–Sn(1)–S(4)	109.07(8)

2.4 Synchrotron X-ray Powder Diffraction

High-resolution SXRPD data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, using an average wavelength of 0.413046 Å. Discrete detectors covering an angular range from -6 to 16° 2 θ were scanned over a 34° 2 θ range, with data points collected every 0.001° 2 θ and a scan speed of 0.01°/s.

The 11-BM instrument uses X-ray optics with two platinum-stripped mirrors and a double-crystal Si(111) monochromator, where the second crystal has an adjustable sagittal bend [37]. Ion chambers monitor incident flux. A vertical Huber 480 goniometer, equipped with a Heidenhain encoder, positions an analyzer system comprised of twelve perfect Si(111) analyzers and twelve Oxford-Danfysik LaCl₃ scintillators, with a spacing of 2° 2 θ [38]. Analyzer orientation can be adjusted individually on two axes. A three-axis translation stage holds the sample mounting and allows it to be spun, typically at ~ 5400 RPM (90 Hz). A Mitsubishi robotic arm is used to mount and dismount samples on the diffractometer. Data were collected at room temperature.

The diffractometer is controlled via EPICs [39]. Data are collected while continually scanning the diffractometer 2 θ arm. A mixture of NIST standard reference materials, Si (SRM 640c) and Al₂O₃ (SRM 676) is used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections are applied for detector sensitivity, 2 θ offset, small differences in wavelength between detectors, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2 θ .

2.5 Rietveld Refinement

Rietveld refinements were performed using GSAS with the EXPGUI interface [40]. The structures of α - and β -Li₂MnSnS₄ that were solved and refined from single crystal X-ray diffraction were used as the starting models for the Rietveld refinement. The starting model for Mn₂SnS₄ [41] in space group *C2/m* was obtained from the Inorganic Crystal Structure Database (ICSD) [42]. This structure seemed to best fit our data. Although the structure of Mn₂SnS₄ has also been reported in the space group *Cmmm* [43,44], refinements using this model were unstable and acceptable refinement statistics could not be achieved. The background was fitted using the shifted Chebyshev polynomial [45]. Peak shapes were modeled using Lorentzian terms, the Lorentzian isotropic crystallite size broadening (LX) and Lorentzian isotropic strain broadening (LY), within the type-3 profile function. Additionally, the unit cell, phase fractions, and Lorentzian anisotropic crystallite size broadening (ptec) terms were refined. Refined unit cell parameters are compiled in Table 3.

Table 3. Results of Rietveld refinements for the α - and β -Li₂MnSnS₄ powder mixture using SXRPD data.

	α -Li ₂ MnSnS ₄	β -Li ₂ MnSnS ₄
Space group	<i>Pna2</i> ₁	<i>Pn</i>
a (Å)	13.6969(2)	6.4188(2)
b (Å)	8.00935(9)	6.8485(3)
c (Å)	6.41931(7)	8.0019(6)
β (°)		89.830(7)

2.6 Optical Diffuse Reflectance UV/Vis/NIR Spectroscopy

Optical diffuse reflectance UV-Vis-NIR data were collected using a Varian Cary 5000 spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory. The sample was ground and placed into a sample holder to a depth of 3 mm. BaSO₄ (Fisher, 99.92%) was used as a 100% reflectance standard. Data were collected from 2500 nm to 200 nm at a scan rate of 600 nm/min. Using the Kubelka-Munk transformation, $\alpha_{KM}/s = (1-R)^2/(2R)$, the raw reflectance (R) was converted to relative absorption (α_{KM}) since the scattering coefficient, *s*, is unknown [46].

2.7 Electronic Structure Calculations

Electronic structure calculations were carried out for α -Li₂MnSnS₄ and β -Li₂MnSnS₄, along with the hypothetical γ -Li₂MnSnS₄, using the full-potential linearized augmented plane-wave approach (FP-LAPW) of density functional theory (DFT) within WIEN2k to solve the Kohn-Sham equations for total energy [47,48,49]. For α - and β -Li₂MnSnS₄, the experimentally determined crystal structures were used as input while the proposed fractional atomic coordinates for the hypothetical γ -Li₂MnSnS₄ in space group *Pmn2*₁ were derived from the Li₂CdSnS₄ [50] structure, which crystallizes in the wurtz-stannite (*Pmn2*₁) structure type. The lattice parameters were obtained by transforming the experimentally determined lattice parameters of β -Li₂MnSnS₄ such that *a*, *b* and *c* axes lengths of β -Li₂MnSnS₄ became the *c*, *b* and *a* axes of γ -Li₂MnSnS₄ [4]. Tables S3 and S4 provide the starting model details for γ -Li₂MnSnS₄.

The Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA) was utilized to account for the exchange correlation energy along with the modified Becke Johnson (mBJ) potential for a better approximation of the bandgap in semiconductors [51,52]. The muffin tin radii (RMT) for Li, Mn, Sn and S were 2.10, 2.47, 2.50, and 2.02 bohr, respectively for α -Li₂MnSnS₄, 2.05, 2.46, 2.50, and 2.01 bohr, respectively for β -Li₂MnSnS₄, and 2.12, 2.50, 2.50, and 2.04 bohr, respectively for γ -Li₂MnSnS₄. Convergence in the self-consistent field (SCF) calculations was achieved when the energy difference in consecutive iterations fell below 0.0001 Ry/unit cell. The RKmax value used to establish the number of plane waves was set to 6.5. The number of k-points used in the full Brillouin zone was 3000, which reduced to 400, 630, and 336 k-points in the irreducible Brillouin zone for α -Li₂MnSnS₄, β -Li₂MnSnS₄, and γ -Li₂MnSnS₄, respectively. The k-point path selected for the band structure plots of all polymorphs was of the primitive unit cell.

Spin polarization was considered in the calculations because of the unpaired electrons in the

manganese atoms. The spin was treated antiferromagnetically by alternating spin-up and spin-down states for the manganese atoms in the unit cell. A geometry optimization of the fractional atomic coordinates was performed on the α -Li₂MnSnS₄ and β -Li₂MnSnS₄ polymorphs. A volume optimization of the lattice parameters was performed on the hypothetical γ -Li₂MnSnS₄ structure, followed by a geometry optimization of the fractional atomic coordinates. Tables S1 and S2 list the optimized fractional atomic coordinates for α - and β -Li₂MnSnS₄, respectively, as compared to those determined by experiment. Tables S3 and S4 provide the calculated lattice parameters and fractional atomic coordinates, respectively, for γ -Li₂MnSnS₄ as compared to the proposed values that were input.

2.8 Attenuated Total Reflectance (ATR) IR Spectroscopy

An IR spectrum for Li₂MnSnS₄ was collected using a Thermo Nicolet 380 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory. The IR spectrum is comprised of 64 scans, from 400 cm⁻¹ to 4000 cm⁻¹. The OMNIC software was used for data collection and analysis. The FT-IR system uses a diamond crystal in optical contact with the sample. Thus, the depth of penetration into the sample is ~2 μ m, which is near the lower limit of the particle sizes for the samples. Therefore, the effect of thickness dependence on the intensity of the measured spectrum is negligible [53].

2.9 Second-order NLO Measurements

A modified Kurtz-Perry powder NLO setup was used to collect data for second harmonic generation [33]. Although we believe the polymorphs to be stable under ambient conditions, a sample was placed into a fused-silica tube that was flame-sealed under vacuum to prevent air and moisture exposure during laser irradiation. The tube was mounted on a Z-scan translation stage via a homemade sample holder. A homemade microcrystalline sample of AgGaSe₂, AgGaSe₂(MC) [54], and a chemically related DLS material, Li₂MnGeS₄ [55], were also measured for comparison purposes.

The SHG responses were measured at room temperature as a function of broadband wavelength. Coherent light, with a wavelength of 1.064 μ m, was initially produced using 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 (HU) H400, in which the input beam was frequency tripled by a sum frequency generation scheme. The beam then entered an EKSPLA PG403-SH-DFG Optical Parametric Oscillator (OPO) composed of four main parts: (i) a double-pass parametric generator, (ii) a single-pass parametric amplifier, (iii) a second harmonic generator (SH), and (iv) a difference frequency generation (DFG) scheme. Output of the OPO was used for measurements with incident wavelengths (λ) ranging from 1.1 μ m to 2.1 μ m in 0.2 μ m increments.

The incident pulse energy was tuned to 17 μ J before being mildly focused onto samples with a spot size diameter of ~0.5 mm using a CaF₂ convex lens. The beam spot size was determined to ensure that i) the SHG signals from powders of random orientations were efficiently generated and properly averaged, and ii) the change in the spot size was minimized as λ was varied over a broadband range since the beam waist, w_0 , at the focus undergoes a significant λ -dependent variation via $w_0 = (\lambda/\pi)(f/\sigma)$, where f and σ are the focal length and the Gaussian width of the incident beam, respectively [56]. The NLO signals from the sample

were collected using reflection geometry by a fiber optic bundle, which was coupled to a selective-grating (1800, 600, and 300 grooves/mm) spectrometer equipped with a charge-coupled device camera (Synapse). The relative SHG signals were spectrally resolved and precisely calibrated using the exposure times as well as the known and measured efficiencies of all optical components. SHG signals from other optical components and surface-induced effects were negligible. Any thermal load on the sample by the laser pulse photon energy tuned below the bandgap was negligible due to its slow repetition rate of 50 Hz.

3. Results and Discussion:

3.1 Crystal Structure Description

The α - and β - $\text{Li}_2\text{MnSnS}_4$ polymorphs crystallize in the lithium cobalt (II) silicate ($Pna2_1$) and wurtz-kesterite (Pn) structure types, respectively. Among the hexagonally derived quaternary diamond-like semiconductors, the wurtz-stannite ($Pmn2_1$) structure is most commonly encountered [57]. While the wurtz-kesterite (Pn) structure is less common, it has been observed for several chemically similar materials, such as $\text{Li}_2\text{ZnSnS}_4$ [58], $\text{Li}_2\text{FeSnS}_4$ [57], $\text{Li}_2\text{ZnGeSe}_4$ and $\text{Li}_2\text{ZnSnSe}_4$ [59]. Notably, the lithium cobalt (II) silicate ($Pna2_1$) structure type is rare and has only been observed in a few instances, e.g., $\text{Ag}_2\text{CdGeS}_4$ [24] and $\text{Li}_2\text{MnGeS}_4$ [60].

The primary difference between these two structure types lies not in small deviations in geometry, but rather exists in the cation ordering. In both structures the anions are arranged in a hexagonally closest packed array where the cations occupy $\frac{1}{2}$ of the tetrahedral holes creating a corner-shared network of tetrahedra. The two structures have identical arrangements of isolated IV-VI₄ tetrahedra in which the I and II cations can reside with different types of ordering.

In Figure 2, the lithium cobalt (II) silicate ($Pna2_1$) structure of α - $\text{Li}_2\text{MnSnS}_4$ (left) and the wurtz-kesterite (Pn) structure of β - $\text{Li}_2\text{MnSnS}_4$ (right) are shown with the cation tetrahedra pointing in the same direction along the c- and a-axes, respectively. If one examines the structures as layers of polyhedra that stack in the ab- and bc-planes for α - $\text{Li}_2\text{MnSnS}_4$ and β - $\text{Li}_2\text{MnSnS}_4$ respectively, the α - $\text{Li}_2\text{MnSnS}_4$ structure has the layer pattern of ABAB and the β - $\text{Li}_2\text{MnSnS}_4$ structure has the pattern A'BA'B. In both structures, the B rows are identical and the A and A' rows are in reverse order to one another. In other words, the A row of α - $\text{Li}_2\text{MnSnS}_4$ houses Li, Li, Sn and Mn from left to right (when viewed along the b-axis) whereas the β - $\text{Li}_2\text{MnSnS}_4$ structure has Mn, Sn, Li and Li from left to right (when viewed along the c-axis). This ordering results in columns of Li and Mn atoms in the α - $\text{Li}_2\text{MnSnS}_4$ structure running along the c-axis where the β - $\text{Li}_2\text{MnSnS}_4$ structure has no such columns.

In order to support the existence of two structures, the collected diffraction data for β - $\text{Li}_2\text{MnSnS}_4$ was also used to solve the structure in the $Pna2_1$ space group (note that the Pn space group has a lower symmetry than the $Pna2_1$ space group); however, this resulted in markedly higher statistics. The systematic absences in the collected data for the α - and β -polymorphs were also carefully analyzed for notable differences. The additional symmetry elements of an a -glide and a 2_1 screw axis in the $Pna2_1$ space group give rise to the additional systematic absences of $h0l$, $h=2n$ and $h00$, $h=2n$. Since the a -axis in the $Pna2_1$ structure corresponds to a doubled b -axis of the Pn structure, the b - and c -axes in the $Pna2_1$ structure correspond to the c - and a -axes in the Pn structure, these systematic absences were converted to $hk0$ $k=2n$

and $0k0$ $k=2n$ for β - $\text{Li}_2\text{MnSnS}_4$. For both the $hk0$ and $0k0$ classes of reflections, an equal number of odd and even k values were found for reflections with significant intensity, indicating that β - $\text{Li}_2\text{MnSnS}_4$ does not possess the a -glide or the 2_1 screw axis.

The averages and ranges of the Li-S bond distances for the two crystallographically unique Li ions in both the α - $\text{Li}_2\text{MnSnS}_4$ and β - $\text{Li}_2\text{MnSnS}_4$ structures agree well with the average Li-S bond distance given in a report by Brunetta et al. [57] in which 40 quaternary DLSSs were analyzed for adherence to Pauling's second rule. The MnS_4 tetrahedra in both the α - and β -structures are nearly identical and the average Mn-S bond distances agree well with other quaternary MnS_4 -containing DLSSs [57]. Of the three cations, Sn^{4+} has the smallest range of bonding distances, which are in agreement with literature reports [57]. While cation disorder is prevalent for the compounds CZTS and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) [25,61], which have recently become popular, these compounds represent special cases, because Cu^+ and Zn^{2+} are isoelectronic and have identical crystal radii. In our case, there is a marked difference in the atomic numbers of Li, Mn and Sn and there is no evidence of disorder. Attempts to model disorder resulted in markedly higher statistics and unreasonable compositions. However, the use of X-ray diffraction data cannot rule out the possibility of a small amount of antisite defects. Cation ordering in the related quaternary DLSSs $\text{Li}_2\text{FeGeS}_4$ (LIGS), $\text{Li}_2\text{FeSnS}_4$ (LITS) and $\text{Cu}_2\text{FeSnS}_4$ has been supported with the use of ^{57}Fe Mössbauer spectroscopy in the case of LIGS and LITS and both ^{57}Fe and ^{119}Sn Mössbauer for $\text{Cu}_2\text{FeSnS}_4$ [62, 63, 64].

Figure 2. Polyhedral representations of α - $\text{Li}_2\text{MnSnS}_4$ (left) and β - $\text{Li}_2\text{MnSnS}_4$ (right) shown down the crystallographic a - and b -axes, respectively. The two structures differ in the arrangement of cations. Both compounds are noncentrosymmetric as all of the tetrahedra point in one direction along the c -axis and a -axis, respectively.

3.2 Synthesis and Laboratory-grade X-ray Powder Diffraction

Attempts to prepare phase-pure α - $\text{Li}_2\text{MnSnS}_4$ and β - $\text{Li}_2\text{MnSnS}_4$ were met with great difficulty. Different heating profiles for direct combination reactions, as well as lithium polysulfide flux reactions using an excess of Li_2S and S were carried out with temperatures ranging from 650 – 800°C and holding times of 72 – 144 hrs. However, one challenge was the competing binary and ternary phases that were often

encountered in reaction products. Phases such as the binary, MnS [65,66] and SnS [67], and the ternary Mn_2SnS_4 [41] could be indexed in laboratory-grade X-ray powder diffraction patterns. An additional difficulty arose from the inability to distinguish the XRPD patterns of the lithium cobalt (II) silicate ($Pna2_1$) structure from that of the wurtz-kesterite (Pn) structure using laboratory-grade XRPD. The small differences in the diffractograms lie in: 1) the slight dissimilarities in calculated intensities of reflections occurring at nearly the same angle, and 2) the additional peaks in the larger sized $Pna2_1$ structure that are very low in relative intensity, ~1% or less. Therefore, due to the striking similarity between the X-ray powder diffraction patterns of the wurtz-kesterite (Pn) and lithium cobalt (II) silicate ($Pna2_1$) structure types, SXPDP was employed.

3.3 Synchrotron X-ray Powder Diffraction

Synchrotron X-ray powder diffraction (SXPDP) was deemed necessary for phase-fraction determination due to the higher resolution and greater intensity. The Rietveld refinement results for the highest quality product are shown in Figure 3. The lattice parameters refined from the SXPDP data are in close agreement with those obtained from single crystal X-ray diffraction, see Table 3. In addition to $\alpha\text{-Li}_2\text{MnSnS}_4$ and $\beta\text{-Li}_2\text{MnSnS}_4$, the diffraction data indicate the presence of at least two unwanted phases, Mn_2SnS_4 [41] and an unknown phase. It should be noted that the unidentified phase is present in only a small amount, as it was not even apparent in the laboratory-grade X-ray powder diffraction data that was initially obtained. A list of unidentified peaks and attempts to index them are explained in the supplemental material, Tables S5-S7. Since the unknown phase could not be indexed with any confidence, the LeBail method could not be employed to fit the extra peaks; therefore, these small peaks result in positive deviations from the calculated pattern and are manifested in the difference plot. However, the largest discrepancy between the observed and calculated diffraction patterns arises from small differences in peak intensities of the strongest Bragg reflections, Figure 3. Performing Rietveld refinements using only $\alpha\text{-Li}_2\text{MnSnS}_4$ ($\chi^2=6.185$, $R_p = 0.1336$ and $wR_p=0.1747$) or only $\beta\text{-Li}_2\text{MnSnS}_4$ ($\chi^2 = 7.179$, $R_p = 0.1420$ and $wR_p = 0.1882$) resulted in reasonable statistics; however, a better fit to the data could be obtained using both polymorphs, see Figure 3. A section of the SXPDP pattern displayed in Figure 4 illustrates that in order to best fit the collected data the Rietveld refinement model should include both $\alpha\text{-Li}_2\text{MnSnS}_4$ and $\beta\text{-Li}_2\text{MnSnS}_4$. When only the α -polymorph is included in the model, refinements show a significant amount of unaccounted intensity. This is demonstrated in the section of data from 12.9 to $13.2^\circ 2\theta$ where a considerable quantity of residual intensity $\sim 13.09^\circ 2\theta$ arises in the difference plot, Figure 4a. Using that same portion of the data, it can be seen that modeling only the β -phase yields a marked amount of residual intensity in the difference plot at ~ 13.055 and $13.09^\circ 2\theta$, Figure 4b. The intensities over this region of 2θ and the entire pattern are accounted for more accurately when both polymorphs are included in the refinement, Figure 4c. The final Rietveld refinement, utilizing both polymorphs resulted in phase fractions of approximately 66.4(2) wt% $\alpha\text{-Li}_2\text{MnSnS}_4$, 20.2(5) wt% $\beta\text{-Li}_2\text{MnSnS}_4$, and 13.34(8) wt% Mn_2SnS_4 .

Figure 3. Results of Rietveld refinement for α - and β - $\text{Li}_2\text{MnSnS}_4$. The collected SXPDP data are plotted with + markers, nearly overlapped by the calculated pattern using the model (line). Expected Bragg reflections are designated with tick marks (|) for Mn_2SnS_4 (13.34(8) wt%), α - $\text{Li}_2\text{MnSnS}_4$ (66.4(2) wt%), β - $\text{Li}_2\text{MnSnS}_4$ (20.2(5) wt %), and from bottom to top. The difference between the collected data and calculated pattern is shown at the bottom of the plot.

Figure 4. Results of Rietveld refinement for (a) only α - $\text{Li}_2\text{MnSnS}_4$, (b) only β - $\text{Li}_2\text{MnSnS}_4$ and (c) both α - and β - $\text{Li}_2\text{MnSnS}_4$. The collected SXRPD data are plotted with + markers, nearly overlapped by the calculated patterns using the models (line). Expected Bragg reflections are designated with tick marks (|) for the α - $\text{Li}_2\text{MnSnS}_4$ phase in part (a), the β - $\text{Li}_2\text{MnSnS}_4$ phase in part (b) and α - and β - $\text{Li}_2\text{MnSnS}_4$ phases from bottom to top, respectively, in part (c). The difference between the collected data and calculated pattern from the model is shown at the bottom of the plot in each part.

3.4 Optical Diffuse Reflectance UV/Vis/NIR and FT-IR Spectroscopy

Optical diffuse reflectance UV/Vis/NIR spectroscopy was performed on a pale-yellow/orange, powdered sample of $\text{Li}_2\text{MnSnS}_4$. In order to estimate the bandgaps of α - and β - $\text{Li}_2\text{MnSnS}_4$, the Urbach tail energy was first determined. Urbach tailing near the absorption edge is a result of defects and disorder within a structure. These imperfections cause the DOS near the valence and conduction band edges to develop tails that extend into the bandgap region. The Urbach tail energy is attained by fitting $\alpha = A \cdot \exp[(E - E_g)/E_u]$, where A is a constant, E is the photon energy, E_g is the bandgap energy, and E_u is the Urbach energy, to a linear section of selected optical data in a plot of the logarithm (log) of absorption versus photon energy [68]. Figure 5 shows the absorption and the log of the absorption as a function of energy for the sample of α - and β - $\text{Li}_2\text{MnSnS}_4$.

The data at energies above the Urbach tail were evaluated to determine if the bandgap was direct or indirect. A direct bandgap will have a sharp absorption edge and an indirect bandgap will have a gradual

onset of absorption [69]. The optical data at energies above the Urbach tail have a wider linear region when rescaled to emphasize the indirect optical transition, i.e. the data plotted as $(\alpha E)^{1/2}$ vs. E has a wider region of linearity than in the plot of $(\alpha E)^2$ vs. E . Thus, if the sample consisted of only one polymorph, it would be clearly assigned an indirect bandgap of 2.58 eV. However, in this case we are hesitant to assign a specific bandgap value and the nature of the transition, considering the sample is a mixture of phases. Therefore, we estimate the bandgap of the two polymorphs to be in the vicinity of ~2.6-3.0 eV, Figure 5. Likewise, in the case of α - and β - $\text{Cu}_2\text{ZnSiS}_4$, an estimated bandgap of 3.0 – 3.2 eV was provided, due to the inability to clearly distinguish two absorption edges in the data [20].

Figure 5. Optical diffuse reflectance data for a powdered sample of α - and β - $\text{Li}_2\text{MnSnS}_4$. The percent reflectance was converted to absorption using the Kubelka-Munk equation and is displayed on the left-hand y-axis. The log of the absorption is shown on the right-hand y-axis. The linear region that corresponds to the Urbach tail is highlighted. The bandgaps of α - and β - $\text{Li}_2\text{MnSnS}_4$ are estimated to be between 2.6 and 3.0 eV.

3.5 Electronic Structure Calculations

The electronic structures of α - and β - $\text{Li}_2\text{MnSnS}_4$ were calculated using the single crystal structure solutions obtained at room temperature, while the electronic structure for the hypothetical polymorph, γ - $\text{Li}_2\text{MnSnS}_4$, was calculated using a proposed wurtz-stannite structure, as explained in section 2.7. Figures S1, S2 and S4 of the supplementary materials provide the spin-up and spin-down band structures of all three polymorphs, while Figure 6 displays the side-by-side comparison of the band structures of α - and β - $\text{Li}_2\text{MnSnS}_4$ in the spin-up configuration. Direct band gaps at the Γ point in the Brillouin zone are revealed for α -, β -, and γ - $\text{Li}_2\text{MnSnS}_4$ polymorphs. The calculated bandgaps of 2.3 eV, 2.6 eV, and 2.3 eV, respectively, are identical for both spin cases of each polymorph. Despite the implementation of the modified Becke-Johnson potential [51,52], which provides more accurate bandgap values for semiconductors, the bandgaps are still slightly underestimated compared with those approximated from the measured optical absorption spectrum. This underestimation is a commonly encountered result of DFT calculations using the PBE-GGA method, as well as several other methods, due to the inexact nature of the exchange-correlation potential energy term [70-72].

To better understand the origin of the bandgaps in the polymorphs, the total and partial density of states (DOS) were calculated. Figure 7 shows the DOS plots for the spin-up and spin-down configurations of

α - $\text{Li}_2\text{MnSnS}_4$. The corresponding plots for β - and γ - $\text{Li}_2\text{MnSnS}_4$ can be found in Figures S3 and S5 of supplementary materials. Comparison of the DOS plots for the spin-up and spin-down configurations shows some pronounced differences, while the DOS from polymorph to polymorph are qualitatively similar and exhibit little variation in their atomic orbital contributions.

Figure 6. The calculated band structures for (a) α - $\text{Li}_2\text{MnSnS}_4$ and (b) β - $\text{Li}_2\text{MnSnS}_4$ in the spin-up configuration. The dotted line denotes the Fermi level (E_f). The calculated bandgaps are direct at the Γ point with values of 2.3 and 2.6 eV for α - and β - $\text{Li}_2\text{MnSnS}_4$, respectively.

Here, the DOS for the spin-up case will be described in detail and, where applicable, variations in the spin-down case will be explained. The states in the valence band for the spin-up configurations from -7.0 to -5.0 eV mainly arise from the Sn s , S s , and S p orbitals and to a much lesser extent the Li s and Li p orbitals. From approximately -5.0 to -1.25 eV, the states mostly originate from the Mn d , and S p orbitals, with the Sn p , Li s , and Li p orbitals providing only weak donations. The valence band maximum, VB_{Max} , in the vicinity of about -1.25 to 0 eV is almost entirely composed of Mn d and S p states; the Sn and Li orbitals provide nearly zero influence in this energy region. The most prominent difference between the spin cases is the orbital contribution of the manganese. In contrast to the DOS of the spin-up configuration, the Mn d states are almost completely absent in the valence band for the DOS of the spin-down configuration. The states at the conduction band minimum, CB_{Min} , ~ 2.5 eV, arise primarily from the Sn s and S p orbitals. Therefore, based on these electronic structure calculations, we propose that the transition across the bandgap observed in the optical spectrum of the α/β - $\text{Li}_2\text{MnSnS}_4$ mixture principally occurs from S $3p$ states at the VB_{Max} to the Sn $5s$ states at the CB_{Min} . These results agree with calculations performed for the chemically similar compounds $\text{Li}_2\text{CdGeS}_4$ [54] and $\text{Cu}_2\text{CdSnS}_4$ [73], where the transition across the bandgap primarily occurs from S $3p$ states at the VB_{Max} to the IV s states at the CB_{Min} . Although the Mn d orbitals play no role in the conduction band states in the spin-up configuration, the states at the CB_{Min} have significant Mn d character in the spin-down case. In all calculations, the states higher in the conduction band of the $\text{Li}_2\text{MnSnS}_4$ polymorphs, from ~ 3.2 to 6 eV, are predominantly derived from Sn s , S p , S s and S p orbitals with minor involvement of Li s , and Li p orbitals. The major contributions of the Li s and p orbitals are mainly spread out over the higher energy conduction band states, greater than 6 eV, due to the highly ionic bonding interaction of lithium with sulfur. Subtle variations in the states near the Fermi level of the α - and β - $\text{Li}_2\text{MnSnS}_4$ polymorphs give rise to the somewhat dissimilar bandgap values. Although the Mn $4d$ states make major contributions to the VB_{Max} and CB_{Min} for the spin-up and spin-down configurations, respectively,

the bandgap observed for the $\text{Li}_2\text{MnSnS}_4$ polymorphs is comparable to other diamond-like semiconductors, where the II cation plays no role in defining the bandgap, for example $\text{Li}_2\text{CdGeS}_4$ (3.15 eV) [50,54] and $\text{Li}_2\text{ZnSnS}_4$ (2.87 eV) [58] that appear pale-yellow and yellow-green, respectively.

The calculated total energies were considered in order to rationalize the difficulty encountered in separately preparing the α - and β - $\text{Li}_2\text{MnSnS}_4$ polymorphs. The calculated total energies of α -, β -, and γ - $\text{Li}_2\text{MnSnS}_4$ were -71496.2870 Ry per unit cell, -35748.1423 Ry per unit cell, and -35748.1082 Ry per unit cell, respectively. Note that since the volume of the α - $\text{Li}_2\text{MnSnS}_4$ unit cell is twice that of the β - and γ - $\text{Li}_2\text{MnSnS}_4$ polymorphs, the total energy obtained for α - $\text{Li}_2\text{MnSnS}_4$ can be halved for the sake of proper comparison. In accordance with the fact that we have no experimental evidence to support the existence of a γ - $\text{Li}_2\text{MnSnS}_4$ polymorph with the wurtz-stannite structure, the calculated total energy of the hypothetical γ -phase registered highest. While the polymorph with the most stable structure, i.e. lowest total energy, was α - $\text{Li}_2\text{MnSnS}_4$, the total energies of all three polymorphs are considered highly similar. These results help to explain the many failed attempts to synthesize the α - and β - $\text{Li}_2\text{MnSnS}_4$ phases in pure form.

Figure 7. The calculated total and partial DOS for the (a) spin-up and (b) spin-down cases of α - $\text{Li}_2\text{MnSnS}_4$. Partial DOS are shown for all crystallographically unique atoms.

3.6 Optical Transparency

Diffuse reflectance UV-Vis-NIR optical spectroscopy in conjunction with ATR FT-IR was used to evaluate the optical transparency of α - and β - $\text{Li}_2\text{MnSnS}_4$. The transparency of the sample, at the ~75% level, extends from ~1 to 25 μm . As shown in Figure 8, the bandgap and the significant Urbach tail region define the lower limit of the transparency window in the vicinity of 0.775 to 0.376 μm (1.6 – 3.3 eV). Although the transparency is quite high, there are some well-defined peaks in the mid-IR that can be tentatively assigned. The peaks around 7 μm (1487 and 1429 cm^{-1}) and below are assigned to -OH stretching due to the presence of water. Several of the peaks at longer wavelengths, 8.8, 10.0, and 11.5 μm (1140, 1000, and 868 cm^{-1}), are attributed to partial oxidation of the compound, since they are in the vicinity of usual M-O stretches. The ^{119}Sn Mössbauer spectrum for the chemically and structurally similar compound, $\text{Li}_2\text{FeSnS}_4$, revealed the compound to have partially oxidized, with one of the doublets assigned to SnO_2 . [62] The peak

at $\sim 21\ \mu\text{m}$ ($475\ \text{cm}^{-1}$) is likely due to a M-S stretch [74-77] of α - and β - $\text{Li}_2\text{MnSnS}_4$.

Figure 8. UV/Vis/NIR (left) and FTIR (right) spectra for α/β - $\text{Li}_2\text{MnSnS}_4$ demonstrating wide optical transparency.

3.7 Second Harmonic Generation

The most pure sample of $\text{Li}_2\text{MnSnS}_4$ was used to perform the wavelength-dependent SHG studies. This sample contained, $\sim 85\ \text{wt}\%$ α/β - $\text{Li}_2\text{MnSnS}_4$ and $\sim 15\ \text{wt}\%$ Mn_2SnS_4 , as well as an unidentified compound according to SXRPD. While the crystal structures of α/β - $\text{Li}_2\text{MnSnS}_4$ are noncentrosymmetric, the structure of Mn_2SnS_4 is centrosymmetric, crystallizing in space group $C2/m$ [41]. Therefore, the presence of Mn_2SnS_4 in the sample will not falsely enhance the SHG response, but rather detract from it. Phase matchability was not determined for this sample due to the presence of impurities; thus, an estimation of the $\chi^{(2)}$ cannot be given. Since the particle size range of the α/β - $\text{Li}_2\text{MnSnS}_4$ sample was small, the SHG response of particles with diameter of $2\text{-}20\ \mu\text{m}$ was measured and plotted in comparison to that of $\text{Li}_2\text{MnGeS}_4$ [55] and AgGaSe_2 (MC) [54].

The α/β - $\text{Li}_2\text{MnSnS}_4$ sample exhibits a moderate SHG response over the entire fundamental range of $1.1\text{-}2.1\ \mu\text{m}$, Figure 9. It should be noted that, for AgGaSe_2 , a significant amount of the SHG signal is absorbed at lower wavelengths, $\lambda_{\text{SHG}} \leq 700\ \text{nm}$, due to its narrower bandgap of $1.83\ \text{eV}$ ($\sim 678\ \text{nm}$). In the case of α/β - $\text{Li}_2\text{MnSnS}_4$ and $\text{Li}_2\text{MnGeS}_4$ the samples undergo a gradual increase in absorption toward the primary absorption edge because of Urbach tailing, Figure 5, which also defines the lower bound of the transparency window, Figure 8. At the highest conversion wavelength, $\lambda_{\text{SHG}}=1050\ \text{nm}$, the α/β - $\text{Li}_2\text{MnSnS}_4$ sample exhibits a response that is $\sim 2\%$ and $\sim 20\%$ that of AgGaSe_2 (MC) and $\text{Li}_2\text{MnGeS}_4$, respectively, Figure 9.

While the SHG response of α/β - $\text{Li}_2\text{MnSnS}_4$ could be significantly stronger if it were prepared as a phase-pure material, these preliminary results together with the fact that the sample has been very difficult to prepare hinder the full assessment of SHG at this time. In this class of materials, more promising candidate IR NLO materials have been recently identified [54,55,73,78,79]. For example, $\text{Li}_2\text{CdGeS}_4$ exhibits a high $\chi^{(2)}$ value ($22.5\text{-}51\ \text{pm/V}$) in competition with commercial materials, an outstanding laser damage threshold and, most importantly, phase-pure samples have been prepared as assessed by high-intensity, high-resolution SXRPD [54]. Likewise, $\text{Li}_2\text{MnGeS}_4$ exhibits an elevated $\chi^{(2)}$ value ($6.5\text{-}15\ \text{pm/V}$) and an

extraordinary laser damage threshold, $> 16 \text{ GW/cm}^2$ ($\lambda=1064 \text{ nm}$, $\tau=30\text{ps}$), while the best sample has been assessed to contain only $\sim 5 \text{ wt\%}$ secondary phases [55]. Neither $\text{Li}_2\text{CdGeS}_4$ nor $\text{Li}_2\text{MnGeS}_4$ exhibit evidence of polymorphism, although the possibility was carefully considered when examining the SXRPD data.

Figure 9. Broadband SHG response for a sample of $\alpha/\beta\text{-Li}_2\text{MnSnS}_4$ (containing $\sim 13 \text{ wt\%}$ Mn_2SnS_4) compared to a microcrystalline sample of AgGaSe_2 and $\text{Li}_2\text{MnGeS}_4$ [55], prepared by high-temperature solid-state synthesis.

4. Conclusion

While some quaternary DLSs are accessible in only one structure type, others, such as the title composition, $\text{Li}_2\text{MnSnS}_4$, have been found to crystallize as polymorphs. The polymorphs in the $\text{Li}_2\text{MnSnS}_4$ system are especially difficult to access in pure form, likely due to the similar ground state energies. This work is further complicated by the fact that SXRPD data is needed for each and every reaction that is prepared since the XRPD patterns of $\beta\text{-Li}_2\text{MnSnS}_4$ with the wurtz-kesterite (Pn) structure and $\alpha\text{-Li}_2\text{MnSnS}_4$ with the lithium cobalt (II) silicate ($Pna2_1$) structure can only be clearly distinguished with the use of high-resolution SXRPD data. It is possible that further synthetic work in this system may even reveal a third polymorph with the wurtz-stannite structure, $\gamma\text{-Li}_2\text{MnSnS}_4$, which was calculated to have a very similar ground state energy as the α - and β -phases. The optical bandgaps of α - and $\beta\text{-Li}_2\text{MnSnS}_4$ are estimated as $\sim 2.6\text{-}3.0 \text{ eV}$. Both α - and $\beta\text{-Li}_2\text{MnSnS}_4$ exhibit noncentrosymmetric structures, and the mixed sample shows a moderate SHG response over a broad range of fundamental wavelengths from $1.1 - 2.1 \mu\text{m}$, as well as a potentially wide region of optical transparency $\sim 1\text{-}25 \mu\text{m}$. It is possible that a series of reactions employing different cooling rates followed by SXRPD of the products could reveal the conditions under which the polymorphs could be isolated; yet this would be a challenging undertaking.

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Figure 1 Color

Figure 1 Grayscale

Figure 2 Color

Figure 2 Grayscale

Figure 4 Color

Figure 4 Grayscale

Figure 5 Color

Figure 5 Grayscale

Figure 6 Color

Figure 6 Grayscale

Figure 7 Color

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Figure 8

Figure 9 Color

Figure 9 Grayscale

Figure 3 Color

Figure 3 Grayscale