Low Thermal Conductivity in Nanocrystalline Zn_3P_2

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Abstract

Semiconductors with low lattice thermal conductivity are important in the search for more efficient thermoelectric materials. The thermal conductivity of nanocrystalline (<7 nm) Zn_3P_2 , fabricated in thin film form by pulsed laser deposition, was measured from 80 K to 294 K. The thermal conductivity of the film showed weak temperature dependence in this temperature range and at 294 K had its highest value of 0.49 W/m K. Although Zn_3P_2 and its family of isomorphic compounds are known to have intrinsically low thermal conductivity, at room temperature the thermal conductivity of this nanocrystalline film is 25% smaller than the calculated minimum thermal conductivity for Zn_3P_2 . Analyzing the thermal conductivity data with the Callaway model revealed that the data could be well fit by considering only boundary scattering and point defect scattering. The boundary scattering length was in good agreement with the film's average crystallite size of 4.1 nm and the magnitude of the point defect scattering required the formation of $\text{V}_{\text{Zn}}\text{-Zn}_i$ pairs from approximately 23% of the Zn sites. It is believed that a large number of point defects are responsible for the intrinsically low thermal conductivity of bulk Zn_3P_2 and therefore the exceptionally low thermal conductivity found in the present study results from the nanometer dimensions of the crystallites. As previous studies have reported high Seebeck coefficients and electronic properties that are insensitive to grain

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boundaries in Zn_3P_2 , the low thermal conductivity observed in the present study suggests that nanocrystalline Zn_3P_2 should be further explored for use in thermoelectric applications.

Keywords: Thermal Conductivity; Zn_3P_2 ; Callaway Model; Nanostructured Materials; Point Defects

1. Introduction

The widespread implementation of thermoelectric type renewable energy sources would be bolstered by the development of efficient devices that are cost effective and formed from earth abundant materials. The efficiency of a thermoelectric is quantified by the dimensionless figure of merit, $ZT = S^2 \sigma T / (\kappa_e + \kappa_l)$, where S is the Seebeck coefficient, σ is electrical conductivity, κ_e is the electronic contribution to the thermal conductivity and κ_l is the thermal conductivity of the lattice. Optimization of ZT is made difficult by the interdependencies that exist between the electronic parameters. As a result, much of the focus when developing more efficient thermoelectrics has been placed on minimizing κ_l and maximizing S . Large reductions of the lattice thermal conductivity have been achieved through nanostructuring (e.g. layered structures, nanowires and nanocrystalline solids¹⁻⁴) and unit cell disorder (e.g. the insertion of “rattlers” in skutterudites and clathrates⁵⁻⁷). In systems with intrinsically low thermal conductivities, if care is taken to produce nanostructure dimensions that are smaller than the dominant phonon mean free paths of the bulk, the resulting thermal conductivities could be exceptionally low.^{8,9}

Zinc-phosphide (Zn_3P_2) is a type $\text{A}^{\text{II}}_3\text{B}^{\text{V}}_2$ semiconductor with a direct optical bandgap of 1.5 eV.¹⁰ It is composed entirely of earth abundant elements and has low production costs.¹¹ The Zn_3P_2 unit cell, shown in Fig. 1, contains 40 atoms and its crystal structure is described as that of a distorted anti-flourite structure, where only three quarters of the voids formed by the

phosphorus tetrahedra are occupied by zinc atoms, leaving the remaining voids vacant.¹² As an example, in Fig. 1 four such vacant voids are highlighted in green. Studies on Zn_3P_2 and its family of isomorphic compounds (Cd_3P_2 , Zn_3As_2 , and Cd_3As_2) have revealed low lattice thermal conductivity as an intrinsic property of the distorted anti-flourite structure.^{13–15} The lowered symmetry of the crystal structure, the resulting distribution of bond lengths, both covalent (56 of the 96 bonds) and ionic (40 of the 96 bonds) in nature, and the large unit cell are all properties shown to correlate with low thermal conductivity materials.^{16–19} Brockway *et al.*²⁰ reported room temperature thermal conductivities of Zn_3P_2 nanowire (30-50 nm diameter) pellets which were 14% higher than the thermal conductivity of Zn_3P_2 samples measured by Nagamoto *et al.*²¹, having much larger crystallites ($\sim 25\text{ }\mu\text{m}$). These findings are contrary to the expectation that increased phonon scattering at the boundaries of the nanostructures should result in a reduction in thermal conductivity. Although there have been numerous reports on the optoelectronic properties of this compound^{10,12,22–24}, stemming from interest for its incorporation in photovoltaic (PV) devices, there are relatively few studies which report on the thermal properties. With previous studies having reported large Seebeck coefficients^{15,20,21,25} (1.8 mV/ K at room temperature reported by Babu *et al.*²⁵) and no appreciable changes to the electrical conductivity in the presence of grain boundaries^{22,25}, further reductions of the lattice thermal conductivity through nanostructuring could be beneficial to increasing the viability of this compound for use in thermoelectric applications. In this work the thermal conductivity of Zn_3P_2 thin films with crystallite sizes less than 10 nm is presented.

Fig. 1. The Zn_3P_2 unit cell. The 40 atom unit cell is tetragonal, with phosphorus and zinc planes alternating along the c-axis. The crystal structure is described as a distorted anti-flourite structure where only three quarters of the tetrahedral voids formed by phosphorus atoms are occupied by zinc atoms. The green tetrahedra highlight several of the tetrahedral voids that are vacant in the unit cell.

2. Experimental Details

2.1 Sample Fabrication

Using a pulsed laser deposition (PLD) system, a 500 nm Zn_3P_2 thin film was deposited onto a silicon wafer on which 100 nm of thermally grown SiO_2 (*th*- SiO_2) had previously been deposited. The PLD system used a KrF excimer laser (Neocera, $\lambda=248$ nm, pulse width=25 ns) with a pulse repetition rate of 10 Hz. For a stoichiometric film, deposition was carried out at room temperature with a pressure of 1.2×10^{-6} Torr using a 99.9% Zn_3P_2 target (Plasmaterials), a laser energy density of 3 J/cm^2 , and a substrate to target distance of 50 cm. Post-deposition processing of the sample included rapid thermal annealing (RTA) in a nitrogen ambient, where

the temperature was increased at 150 K/s, held at 773 K for 120 s and then decreased to room temperature at 20 K/s. Annealing at higher temperature or for longer durations resulted in the sample deviating from stoichiometry.

2.2 Structural Characterization

X-ray diffraction (XRD) data for the film was collected at room temperature using a PANalytical X'Pert Pro Materials Research Diffractometer with a Cu-K α source ($\lambda = 1.54 \times 10^{-10}$ m) in the grazing incidence configuration. The resulting XRD pattern was used for phase identification, determination of the lattice constants and, with subsequent Scherrer Analysis, determination of the crystallite sizes of the film. The crystallite sizes and morphologies were observed using a high resolution transmission electron microscopy (HRTEM) system (JEM 2100F from JEOL).

2.3 Thermal Conductivity Measurement

Thermal conductivity measurements were made using the 3ω -method popularized by Cahill for measurements on bulk solids and later extended to measurements of thin films.^{26,29} In this work the heater line was fabricated by electron beam evaporation of a 3 nm chromium adhesion layer and a 50 nm gold layer, followed by subsequent photolithographic patterning to the desired heater line dimensions of 1000 μm x 20 μm . The electrical conductivity of the Zn_3P_2 film was large enough to cause spurious 3ω signals. It was necessary to deposit an electrically insulating film between the Zn_3P_2 sample and the metal line to prevent this. Using an AJA Orion sputter deposition system, a 180 nm amorphous SiO_2 ($a\text{-SiO}_2$) film was deposited to serve as the electrical insulation between the Zn_3P_2 film and metal line. As the effect of multiple thin films on a substrate are additive, the thermal conductivity of this $a\text{-SiO}_2$ film, as well as that of the *th*-

SiO₂ film, were measured independently in order to later subtract their contributions to the overall measurement. The thermal conductivity and thermal diffusivity of single crystal silicon from Ref. 30 were used to calculate the thermal response of the substrate.

3. Results

Fig. 2. The XRD profile for Zn₃P₂. The angle used for the grazing incidence scan was $\omega=0.60^\circ$. The sample is polycrystalline and displays the characteristic (202), (220), and (224) peaks of tetragonal Zn₃P₂, along with other minor Zn₃P₂ peaks.

3.1 Structural Characterization

The XRD pattern shown in Fig. 2, where an incident angle of $\omega=0.60^\circ$ was used, indicates that the sample is polycrystalline with no preferential orientation, displaying the characteristic (202), (220), and (224) peaks of tetragonal Zn₃P₂ along with other minor Zn₃P₂ peaks (JCPDS Card: 01-073-4212). From the location of the (202), (220), (224), and (305)

peaks, the average unit cell dimensions are calculated as $a = b = 8.10 \text{ \AA}$ and $c = 11.43 \text{ \AA}$. The accepted values for the Zn_3P_2 unit cell are $a = b = 8.09 \text{ \AA}$ and $c = 11.41 \text{ \AA}$.³¹ Using a Pseudo-Voigt model fitting function, the (202), (220), and (224) peaks were fit and the crystallite sizes were determined according to the Scherrer equation³²:

$$L = \frac{K \lambda}{B \cos(\theta)} \quad (1)$$

where L is the crystallite size, K is the Scherrer constant (taken as 0.94³³), B is the peak width in radians and 2θ is the location of the peak maximum. The fittings resulted in average crystallite sizes of 3.0 nm, 2.9 nm, and 6.3 nm for the (202), (220), and (224) peaks, respectively, giving an overall average crystallite size of 4.1 nm. The HRTEM image in Fig. 3 also indicates the existence of multiple crystallites with sizes in the <10 nm regime and varying crystallographic orientations in the Zn_3P_2 film, in good agreement with the XRD data.

Fig. 3. The HRTEM image of the Zn_3P_2 film. Many crystallites with a variety of interplanar spacings can be seen, having dimensions that are found to be in good agreement with sizes determined from the analysis of the XRD peaks.

3.2 Thermal Conductivity

Fig. 4. The thermal conductivity data for Zn₃P₂. The thermal conductivity data for the Zn₃P₂ PLD thin film of the present study, measured from 80 K to room temperature, are shown as green circles. The red squares are thermal conductivity data taken from Nagamoto *et al.*²¹ for samples of SPS polycrystalline Zn₃P₂. The blue inverted triangles are thermal conductivity data taken from Brockway *et al.*²⁰ for Zn₃P₂ nanowire (30-50 nm in diameter) pellets, consolidated through hot uniaxial pressing.

In Fig. 4, the temperature dependent thermal conductivity data of the PLD Zn₃P₂ thin film are shown as green circles. The overall uncertainty in the reported data, more than half of which comes from the uncertainty in the measurement of the film thickness, is indicated by the error bars. To the authors' knowledge this is the first reported data on the thermal conductivity of Zn₃P₂ thin films. The thermal conductivity of the Zn₃P₂ film shows weak temperature

dependence in the temperature range measured. The thermal conductivity of 0.49 W/m K at 294 K is the maximum value observed in the temperature range measured. For comparison, also shown in Fig. 4 are data from other reports on the thermal conductivity of Zn_3P_2 . Nagamoto *et al.*²¹ measured the thermal conductivity of SPS polycrystalline Zn_3P_2 samples, which were fabricated from solid-state reacted powders, shown as red squares in Fig. 4. Brockway *et al.*²⁰ used hot uniaxial pressing to consolidate Zn_3P_2 nanowires synthesized through reactive vapor transport of red phosphorus onto zinc foils, shown as blue inverted triangles in Fig. 4.

4. Discussion

In Fig. 4, it can be seen that at room temperature the Zn_3P_2 thin film sample measured in this work falls a factor of 3 below that of the Zn_3P_2 SPS powders and Zn_3P_2 nanowire pellet. It is expected that a main reason for the observed reduction in thermal conductivity between the Zn_3P_2 film and the other samples results from increased boundary scattering, where for instance the nanowires measured by Brockway *et al.*²⁰ were 30-50 nm in diameter as compared to the 2.9-6.3 nm crystallite sizes of the current study. Although the crystallite sizes for the SPS Zn_3P_2 powders measured by Nagamoto *et al.*²¹ were unavailable, during fabrication the powders were passed through a 500 mesh sieve (25 μm openings) before SPS at high temperature, suggesting the presence of crystallites which are at least 25 μm in diameter. As previously mentioned, it is peculiar that the thermal conductivity of the Zn_3P_2 nanowire pellet is found above that of the SPS microcrystals, where the electronic component of the thermal conductivity was negligible in both studies, while (as it will be shown) nanostructuring produces significant reductions in the thermal conductivity of the Zn_3P_2 film. Also of interest is the weak temperature dependence observed in the thermal conductivity of the Zn_3P_2 film. A temperature independent thermal conductivity is

typically observed in glasses and is known to occur in grossly disordered crystalline solids, for example with large concentrations of point defects.³⁴ Given that the XRD pattern in Fig. 2 clearly indicates that the film is crystalline, the latter seems to be a better explanation.

4.1 Callaway Model

To further explore the thermal conduction limiting mechanisms in the Zn_3P_2 thin film, the thermal conductivity data were fit using the Callaway model with considerations of boundary (τ_B), point defect (τ_{PD}), umklapp (τ_U), and normal (τ_N) scattering processes, where τ_i are the associated relaxation times for each process.³⁵ From the Wiedemann-Franz law and the room temperature electrical conductivity of $128 (\Omega \text{ m})^{-1}$ (as determined from the charge carrier concentration of $2 \times 10^{18} \text{ cm}^{-3}$ and charge carrier mobility of $4 \text{ cm}^2/\text{V} \cdot \text{s}$), the electronic contribution to the thermal conductivity is found to be negligible and the total thermal conductivity is given almost entirely by the lattice component. Callaway gives the thermal conductivity of the lattice as

$$\kappa_L = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \tau_C \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (2)$$

where $x = (\hbar\omega/k_B T)$ is a dimensionless variable, ω is the phonon frequency, k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, v is the average sound velocity, $\Theta_D = v(\hbar/k_B)(6\pi^2 n)^{1/3}$ is the Debye temperature, $n = 5.31 \times 10^{28} \text{ m}^{-3}$ is the atomic number density, and τ_C is the combined relaxation time. From Ref. 36 the longitudinal and transverse sound velocities for Zn_3P_2 are $v_l = 5290 \text{ m/s}$ and $v_t = 2000 \text{ m/s}$, respectively, from which the average sound velocity and Debye temperature are calculated as 2269 m/s and 254 K , respectively. Matthiessen's rule for addition of the relaxation times gives the combined relaxation rate, τ_C^{-1} , as

$$\begin{aligned}
\tau_C^{-1} &= \tau_B^{-1} + \tau_{PD}^{-1} + \tau_U^{-1} + \tau_N^{-1} \\
&= v/L_C + A \omega^4 + B1 \omega^2 T e^{-\Theta_D/T} + B2 \omega^2 T
\end{aligned}
\tag{3}$$

where L_C is the Casimir length and A, B1, and B2, are the coefficients for point defect, umklapp and normal scattering processes, respectively.

Fig. 5. Thermal conductivity models. The thermal conductivity data for the Zn_3P_2 thin film are shown as green circles. The best fit to the data found using the Callaway model with considerations of boundary, point defect, umklapp, and normal phonon scattering processes is shown as a black line with large dashed. The Callaway model was made to also include the effect of resonant phonon scattering processes and the resulting best fit to the data is shown as a solid red line. The minimum thermal conductivity for Zn_3P_2 is also shown, and is given as a blue line with small dashed.

The fitting parameters that resulted in the best fit to the data, as determined through the minimization of χ^2 , were: $L_C \rightarrow 2.0$ nm, $A \rightarrow 3.2 \times 10^{-41}$ s³, $B_1 \rightarrow 0$ and $B_2 \rightarrow 0$, for which the resulting fit is shown in Fig. 5 as a dashed black line. The fit achieved overlays well with the thermal conductivity data of the Zn₃P₂ film, shown in green circles, and it is interesting to note that the inclusion of both phonon-phonon scattering processes, normal and umklapp, was unnecessary to fit the data in the temperature range considered. The Casimir length, which generally has the dimensions of the film crystallite size³⁷, determined from the fitting is in good agreement with the average crystallite size of 4.1 nm determined from Scherrer analysis. It is then interesting to consider the phonon scattering that arises from point defects.

4.1.1 Point Defect Phonon Scattering

If boundary scattering were the only phonon scattering process included in the Callaway model, the thermal conductivity would become a factor of 4.5 larger at room temperature, indicating the significant reduction in thermal conductivity that results from the presence of point defects. As measured by Energy Dispersive X-ray analysis (EDX), the Zn₃P₂ film is stoichiometric. It is therefore difficult to believe that there exists a significant number of vacancies or interstitials associated with a deficiency or excess of constituent elements, respectively. It is also possible that there are instead antisite defect pairs, being Zn_P and P_{Zn}, but Demers *et al.*³⁸ determined that such defects are too unstable and would result in the formation of Zn_i-V_P and P_i-V_{Zn}, respectively. Given the atomic density of the unit cell, the space needed for even a moderate number of defect pairs of this type is also unavailable. Furthermore, the lattice constants calculated using the XRD data for the Zn₃P₂ film were in good agreement with the accepted values, indicating the absence of large distortions to the unit cell. The most

energetically favorable defect types in Zn_3P_2 are that of phosphorus interstitials, P_i , and the less energetically favorable zinc vacancy, V_{Zn} .³⁹ As there are considerably more sites (8 tetrahedral voids per unit cell) in which a Zn_i can reside (necessary for accommodating a V_{Zn} given that the sample is stoichiometric), as compared to the lone suitable site per unit cell for accommodating a P_i ³⁹, the point defect scattering that results from the formation of a $\text{V}_{\text{Zn}}\text{-Zn}_i$ pair is considered.

The point defect scattering parameter was given by Klemens⁴⁰ as

$$A = \frac{V_0 \Gamma}{4\pi v^3} \quad (4)$$

where V_0 is the volume per atom, v is the average velocity, and Γ is the disorder scattering parameter. Γ is given by the sum of two terms which quantify the effects of mass disorder (Γ_M) and strain field (Γ_S) scattering that result from a point defect. However, because of the uncertainty associated with determining the effective radii of these defects, which is required for calculation of the strain field scattering, only mass disorder scattering will be considered in the following. Furthermore, from the density functional theory (DFT) work of Demers and van de Walle³⁸ on the defect types in Zn_3P_2 , there is reason to believe that the effective radii difference between a Zn ion and V_{Zn} in Zn_3P_2 may be less than 5%, which would result in a negligibly small Γ_S term. Slack⁴¹ developed an expression for the mass disorder scattering parameter for a compound, which in the case of a binary compound of the form A_xB_y is given as

$$\Gamma_M(\text{A}_x\text{B}_y) = \frac{x}{x+y} \left(\frac{\bar{M}_A}{\bar{M}} \right)^2 \Gamma_M(A) + \frac{y}{x+y} \left(\frac{\bar{M}_B}{\bar{M}} \right)^2 \Gamma_M(B) \quad (5)$$

where $\bar{M}_i$ are the average masses at the i th ($i = A, B$) site in the unit cell, and $\bar{M}$ is the average mass of all atoms in the unit cell. The $\Gamma_M(i)$ are the scattering coefficients associated with the mass disorder present at the i th site and are given by

$$\Gamma_M(i) = \sum_j f_j \frac{(M_j - \bar{M}_i)^2}{(\bar{M}_i)^2} \quad (6)$$

where f_j are the fractional concentrations of defects with mass M_j at the i th site and $\bar{M}_i$ is the average mass of the i th site. If for example there is no disorder on site B, $\Gamma(B) = 0$.

From (6) it is clear that the zinc vacancy is the single most effective mass disorder type point defect in Zn_3P_2 , as it represents the largest mass difference. Considering only this defect type, with (5) and (6) it is found that 23% of the Zn lattice sites would necessarily be occupied by vacancies to achieve the strength of point defect scattering found from fitting to the Callaway model. The reader is reminded that this result represents an upper limit to the magnitude of Γ_M , as the Γ_S associated with these Zn vacancies and possible disorder on P sites may also contribute to the total point defect scattering.

4.1.2 Resonant Phonon Scattering

It is expected that in the stoichiometric Zn_3P_2 film a large number of V_{Zn} defects should be accompanied by a proportionate number Zn_i defects. Furthermore, it is known that interstitial type defects will have associated with them an additional mechanism by which phonons can be scattered in a solid.⁴² Most notably, in the case of filled clathrates and filled skutterudites a “guest” atom or molecule is loosely bound and free to oscillate (or “rattle”) within a void created by the host structure, and can lead to a marked reduction in thermal conductivity.^{6,43–45} The modes associated with these “rattlers” are highly localized and as a result have been modeled as Einstein oscillators.^{46,47} A resonant type interaction of the “rattlers” with the low frequency normal modes of the solids has, with great success, been modeled using the resonant phonon scattering formalism put forth by Pohl.^{7,48–51} Pohl provides an additional resonant scattering term to be included in the total phonon relaxation rate, given as

$$\tau_{res}^{-1} = \frac{C \omega^2}{(\omega_0^2 - \omega^2)^2} \quad (7)$$

where ω is the phonon frequency, C is a fitting parameter that is proportional to the number of resonant scatterers, and ω_0 is the resonant frequency.

The total relaxation rate of (3) was made to include the additional resonant scattering term given by (7) and the data were refit, however having the boundary scattering term fixed at its previously determined value. The resulting fitting parameters are: $L_C \rightarrow 2.0$ nm, $A \rightarrow 2.0 \times 10^{-41}$ s³, $B_1 \rightarrow 0$, $B_2 \rightarrow 0$, $C \rightarrow 2.8 \times 10^{37}$ s⁻³ and $\omega_0 \rightarrow 1.4 \times 10^{13}$ rad/s and the resulting fit is shown in Fig. 5 as a solid red line. With the inclusion of the resonant scattering term, a slightly better fit is achieved in the low and high temperature ranges of the thermal conductivity data. A significant feature of this result is that the point defect scattering term remains close to its original value, even with the inclusion of the resonant scattering term. The previous analysis for point defect scattering is still applicable and it is encouraging that the data is well described by the fit after accounting for the presence of interstitial atoms, albeit whose effect on the thermal conductivity is small in the temperature range measured. Klitsner and Pohl⁵² have used

$$\nu_{dom} = \left(90 \frac{GHz}{K} \right) T \quad (8)$$

to approximate the frequency of the phonons that dominate thermal transport at a given temperature, where ν_{dom} is the phonon frequency in Hz. For the 2.2 THz resonant frequency determined from the Callaway model fitting, (8) suggests that the effect of resonant scattering would be greatest near 24 K. Therefore an extension of the thermal conductivity measurements to much lower temperatures would be necessary to gain additional insight about the resonant scattering in this system.

4.1.3 The Origin of High Concentrations of Point Defects

As it draws many similarities to the considerations of the present study we mention briefly the semiconducting compound β -Zn₄Sb₃. β -Zn₄Sb₃ is in a class of materials known as “phonon-glass electron-crystals”⁵³ and has one of the highest thermoelectric figures of merit, ZT, in the temperature range of 473-673 K, owing to its exceptionally low lattice thermal conductivity (Room temperature values from 0.65 W/m K for bulk to 0.10 W/m K for thin films have been reported.)⁵⁴⁻⁵⁶ Synchrotron powder diffraction resolved electron density analysis and DFT calculations have established that this low lattice thermal conductivity results from as many as 20% of the Zn atoms sitting on three distinct interstitial sites with a large percentage of the 36 Zn lattice sites being left vacant.^{9,55,57,58} The Zn vacancies provide highly effective centers for point defect scattering and the three unique interstitial sites should have associated with them three unique resonant frequencies that are able to resonantly scatter long wavelength phonons. A study of the temperature dependent occupancy of the Zn lattice site and the Zn_i site revealed that occupancy of the Zn_i site was highly favored at high temperature. Furthermore, it has been shown that rapid cooling after the annealing of β -Zn₄Sb₃ prevented the room temperature equilibrium population of the Zn lattice site from being established.⁵⁹ This is consistent with other reports of rapid cooling after high temperature annealing during the fabrication of β -Zn₄Sb₃ samples in which low thermal conductivity was reported.⁵⁴

In an XRD study coupled with structure refinement software, Zanin *et al.*⁶⁰ have pointed out that of the four tetrahedra in Zn₃P₂, two are distinctly occupied by two of three distinct Zn atoms of the lattice. Furthermore, there is an equal probability for the remaining Zn atom, known as the Zn(2) atom, to reside in either of 2 remaining voids in the lattice leaving the other as a vacant void. Figure 1 helps to illustrate this idea where the Zn(2) atom is shown being

bonded tetrahedrally to the surrounding P atoms, and the adjacent void sites, highlighted by the green tetrahedra, are the equivalent positions in which the Zn(2) atom can reside. Although Zanin *et al.*⁶⁰ state that in equilibrium only one of these two sites is continuously occupied throughout the crystal by the Zn(2) atom, their observation comes as a result of the structure refinement software producing an equilibrium state in the Zn₃P₂ system. In the present study, the RTA process subjected the Zn₃P₂ film to annealing at 773 K for 120 s, followed by rapid cooling at 20 K/s to room temperature. It is likely that the RTA process disturbs the equilibrium configurations of the Zn(2) and vacancy void sites and with the rapid cooling that follows, reestablishment of the equilibrium populations of these two sites is not possible. This would then result in a large number of V_{Zn}-Zn_i pairs, similar to what has been observed in β -Zn₄Sb₃.

4.2 Minimum Thermal Conductivity

The low thermal conductivity of the Zn₃P₂ film, as well as its weak temperature dependence for the entire temperature range measured, make it interesting for comparison to the minimum thermal conductivity model formulated by Slack²⁷ and extended by Cahill and Pohl²⁸. The model proposes that the phonon mean free path (MFP) is half the wavelength of a normal mode, $\lambda/2$, and that the phonon dispersion relationship is that of the Debye model ($\omega = v (2\pi/\lambda)$, where v is the speed of sound and λ is the phonon wavelength). The resulting minimum thermal conductivity is given by

$$\kappa_{min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \quad (9)$$

where i indicates the polarization (l and t for the longitudinal and transverse polarizations, respectively) of the three sound modes, v_i is the sound velocity, n is the number density of atoms, and Θ_i is the Debye temperature given by $\Theta_i = v_i(\hbar/k_B)(6\pi^2 n)^{1/3}$. Equation (10) was

evaluated using the velocity and atomic density values previously mentioned for use in the Callaway model.

The resulting minimum thermal conductivity curve is shown in Fig. 5 as a blue line with small dashed, where it can be seen that it lies above the thermal conductivity of Zn_3P_2 film for all but the lowest temperatures at which measurements were made. The rapid fall off in the minimum thermal conductivity at lower temperatures is expected because of the growing importance of phonons with long MFPs in real solids. The fact that the thermal conductivity of the Zn_3P_2 film lies at all below the minimum thermal conductivity, where it is 25% smaller at room temperature, is peculiar. If the minimum thermal conductivity calculation is extended to 800 K, it has a value of 0.72 W/m K and the thermal conductivity of the samples measured by Brockway *et al.*²⁰ and Nagamoto *et al.*²¹ would lie above it. This indicates that falling below the minimum is not an intrinsic property of Zn_3P_2 . Since the formulation of the minimum thermal conductivity concept, there have been few reports on solids (amorphous or crystalline, where in fact crystallinity seems to be a requirement for falling below the “glassy limit”⁶¹) that are found to have thermal conductivities that fall below this limit. Notably, systems that have been identified as such include some layered films, copper based so called “phonon-liquid electron-crystals” (PLECs), and some nanocrystalline (<30 nm crystallites) solids.^{61–66}

4.2.1 Thermal Conductivity Below the Minimum

As it relates to the present study, the observations of Feser *et al.*⁶⁶ of thermal conductivities in some CdSe thin films with grain sizes of 3-6 nm falling below the minimum thermal conductivity are particularly interesting. Although the exact cause for the thermal conductivities of their study falling below the minimum was not determined, Feser *et al.*⁶⁶, based

on considerations of the phonon dispersion relations of CdSe, were able to reject ballistic phonon transport (often used to explain anomalous reductions in thermal conductivity observed in crystals with boundary dimensions on the order of dominant phonon MFPs⁶⁷) as the cause. Furthermore, they reason that the CdSe phonon dispersion relations illustrate the inconsequential nature of thermal transport from optical and short wavelength acoustic phonons. Thus, the minimum thermal conductivity model can overestimate the thermal conductivity of a solid when, for each polarization, a single group velocity is assumed for all modes.

The 40 atom unit cell of Zn₃P₂ results in 120 phonon branches (3 acoustic and 117 optical) that highly complicate the details of thermal transport. To the best of the authors' knowledge, there is at present no publication of the phonon dispersion relations for Zn₃P₂. The unavailability of the phonon dispersion relations makes it difficult to elucidate the exact cause for the thermal conductivity of the nanocrystalline Zn₃P₂ film falling below the "glassy limit", and highlights the need for such a study. Given that low thermal conductivity has been observed in every report on Zn₃P₂ and its family of isomorphic compounds, it is likely that a relatively short MFP for the dominant heat carrying phonons is an intrinsic property of the crystal structure. Furthermore, that the effect of nanostructuring produced no reduction in the room temperature thermal conductivity of the nanowire pellets in the study of Brockway *et al.*²⁰ suggests that these boundary effects occur at length scales smaller than 30-50 nm. If the largest room temperature thermal conductivity reported for Zn₃P₂ (~2.5 W/m K by Masumoto *et al.*¹⁵) is used as an estimate for the bulk value, the Zn₃P₂ film of the present study has the value $\kappa_{Film} = 0.2 \kappa_{Bulk}$ at room temperature. If it is assumed that the phonon MFP is independent of frequency and that the scattering processes of the film are equivalent to that of the bulk, with the effect of additional boundary scattering given by Matthiessen's rule, we find that

$$\frac{\kappa_{Film}}{\kappa_{Bulk}} = \frac{L_{Film}}{L_{Film} + L_{Bulk}} \quad (10)$$

where κ_{Film} and κ_{Bulk} are the thermal conductivities of the film and bulk, respectively, and L_{Film} and L_{Bulk} are the MFP due to the additional boundaries from nanostructuring in the film and the MFP of bulk, respectively. If the largest crystallite size (6.1 nm) determined in this study is used for L_{Film} , we find that the MFP of bulk Zn_3P_2 is 24.4 nm. From this result, the nanowires of Brockway *et al.*²⁰ would be too large to reduce this MFP, but the <7 nm crystallites in the film of the present study would greatly reduce it.

5. Conclusion

A nanocrystalline Zn_3P_2 thin film was fabricated using PLD and crystallized by RTA at 773 K for 120 s. XRD analysis and HRTEM indicated that the film was polycrystalline with an average crystallite size of 4.1 nm. The thermal conductivity of the Zn_3P_2 film was measured from 80 K to 294 K using the 3ω method. The thermal conductivity in this range showed weak temperature dependence and at 294 K had its highest value of 0.49 W/m K. The thermal conductivity data were well fit with the Callaway model, where only boundary and point defect phonon scattering processes were initially needed to achieve a good fit. The boundary scattering term was in good agreement with the average crystallite size. From considerations of the formation energies and site availabilities, the point defect scattering is believed to have its origins in 23% of Zn sites being occupied by vacancies, with a commensurate number of interstitial sites being occupied by Zn atoms. The inclusion of resonant phonon scattering processes in the Callaway model, to account for phonon scattering by Zn interstitials occupying lattice voids, also resulted in a good fit to the data. From previously reported results on structure refinement in Zn_3P_2 , it is suggested

that the formation of a high number of $V_{Zn}-Zn_i$ pairs is made possible by the Zn(2) atom having an equal probability of occupying a lattice site or void. The thermal conductivity of the Zn_3P_2 film fell below the minimum thermal conductivity for all but the lowest temperatures measured. The unavailability of a phonon dispersion for Zn_3P_2 makes elucidation of the thermal conduction that arises from its 120 phonon branches difficult. With such remarkably low thermal conductivity not having been observed in previous reports on Zn_3P_2 , it is believed that the findings of present study result from the <7 nm crystallite sizes of the Zn_3P_2 film.

As a number of authors have previously reported that there is no appreciable change in the electrical conductivity of Zn_3P_2 in the presence of grain boundaries^{22,25}, the reductions in thermal conductivity achieved through nanostructuring in this study is promising for increasing the viability of Zn_3P_2 's use in thermoelectric applications. As future work may involve the tailoring of point defects to achieve better electronic conduction properties for improved thermoelectric performance, we note that Zn interstitials were found to have only a small effect on the thermal conductivity and as this defect type is believed to act as an electron donor³⁸, it is suggested that Zn deficient compositions should be desirable for an increase in p-type conductivity while having a negligible effect on the thermal properties.

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