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Experimental study of molten tin sulfide thermal conduction

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Abstract.

Molten thermoelectrics are proven candidates to harvest waste-heat from high-temperature industrial operations in the form of electrical power. However to date, the role of thermal conductivity remains to be evaluated in order to evaluate the overall efficiency. Herein, possible modes of heat transfer and their analysis for such molten semi-conductor are presented. Experimental estimates of thermal conductivity obtained on a power generation thermoelectric device operated with molten tin sulfide at temperature in excess of 900°C are then presented. Results of the simulation of the temperature profile, the fluid mechanic model and electrical power performance show a key role of natural convection and a minor role of radiative heat transfer, and indicate a possible variation in transport properties of tin sulfides around 1000°C.

Keywords. molten semiconductors, thermal conductivity, thermoelectric, tin sulfide, natural convection

1. Introduction

Regardless of the progress made in the past decades for solid-state thermoelectric materials, thermoelectric waste-heat recovery for industrial processes at high temperature ($T > 650^\circ\text{C}$) remains a key challenge due to the unique combination of high temperature, large surface area and low heat-flux.¹

Thermoelectric generation using molten semiconductors from high temperature industrial processes has been proposed, using high melting point and low-cost materials. In particular, essential properties such as Seebeck coefficient and electrical conductivity for molten chalcogenides have been reviewed, confirming the potential utility of these materials for thermoelectric applications.^{2–11} We recently investigated experimentally such properties for molten SnS and constructed a laboratory-scale thermoelectric generator that successfully and continuously operates at a mean temperature (arithmetic mean of hot and cold temperature) in excess of 1000°C .¹ The cell consists of axisymmetric, concentric graphite electrode cylinders, schematically shown in Figure 1, where an inner heating element dissipates heat through a graphite annular space containing the molten thermoelectric material (experimental details available in ref 1). The study confirmed promising performance for molten SnS and demonstrated power generation.

Figure 1 also shows the anticipated liquid heat and momentum transfer due to natural convection in the annulus space of the thermoelectric test cell studied in reference 1.

Figure 1 Schematics (not to scale) showing a half-cross-sectional view of the concentric cylinders model temperature boundary conditions and the corresponding momentum transfer in the liquid due to natural convection (left). Right shows a cross-sectional view in perspective, showing the heating element, the axisymmetric axis, the inner hot surface (orange) and outer cold surface (blue) in the annulus space of the thermoelectric test cell. The top and bottom liquid boundaries are assumed to be adiabatic. The gap between the external surface of the heating element and the inner hot surface is 2.7mm, the inner graphite cylinder thickness is 5mm, the outside graphite cylinder thickness is 10mm.

However, the thermal conduction properties of molten SnS remain missing and are critical towards a better understanding of the materials challenge behind power generation using molten thermoelectrics at high temperature. This paper therefore aims at the evaluation of the heat transfer mechanisms of molten semiconductors. More precisely, we study molten SnS as representative molten thermoelectric materials and use experimental results obtained in the concentric cylinder design of Figure 1, a configuration that provided the initial demonstration of possible power generation.

Three fundamental heat transfer modes are reported for materials; conduction, radiation and convection.¹² For solid-state thermoelectric materials operating at low temperature, only conduction is considered relevant, with extensive solid-state materials science effort toward its optimization for thermoelectric applications.^{13–17} For molten semiconductors, and due to their fluid nature, convection is likely a non-negligible contribution in particular considering the large temperature gradient anticipated for thermoelectric generation. Combined with thermal expansion, density differences are likely and would drive *natural* convection. In addition, radiative heat transfer is likely important at high temperature given the strong temperature dependence (T^4) of thermal emission based on Stefan-Boltzmann law. We briefly review below available methods to evaluate intrinsic thermal conduction, prior to discussing how to access the additional modes specific to high temperature molten materials.

1.1 Intrinsic thermal conduction

Laser pulses into a material, and their corresponding transient temperature responses are commonly used to determine thermal diffusivity. Knowledge of density and heat capacity enables to access thermal conductivity, as shown for thin material sample by Parker, Jenkins et al.,¹⁸ a method named Laser Flash method. Its reliability has been extensively verified with various solid materials (e.g. metals, ceramics, semiconductors, etc.^{18–22}). The method was also broadly used to measure thermal diffusivity of liquid materials due to its non-contact nature and hence robustness.²³ For example, molten Ge and Si,²⁴ molten Te,²⁵ molten Ni,²⁶ molten Hg,^{27,28} molten Sn,²⁹ various molten salts³⁰, various molten oxides³¹ were all studied by Laser Flash method, and the results showed good agreement with previous reports. Mills, Monaghan et al.²³ have pointed out that molten materials are likely to develop natural convection 1 to 2 seconds after the onset of a laser pulse, which could skew the results. In practice, the experimental time scale of Laser Flash method for molten materials to prevent natural convection shall be on the order of hundreds of milliseconds. However, the key practical challenges of this method for molten semiconductors with high melting point (e.g. molten sulfides) are the compatibility between the crucible material and the corrosive melt, and the suppression of excess vapor pressure, which could damage the laser source and the temperature sensing apparatus.

In addition, the conversion from thermal diffusivity (δ) to thermal conductivity (κ), as shown in the following equation,

$$\delta = \frac{\kappa}{\rho C_p} \quad (1)$$

relies on the availability of heat capacity (C_p) and density (ρ) which are not readily available for high temperature molten semiconductors. Shall all these practical challenges be resolved; Laser Flash method would be considered a promising technique to quantify intrinsic thermal conduction and radiative thermal conduction by isolating the contribution from natural convection. By combining its results with apparent thermal conductivity measurement under convective condition, such as presented

herein and in details in reference³² for a given geometry, the effective thermal conductivity from natural convection for that specific geometry can be obtained.

The few prior investigations^{6,33–35} show that the intrinsic thermal conductivities of molten semiconductors (including sulfides and selenides) are approximately 1 to 2 W m⁻¹ K⁻¹. The assumption that the intrinsic thermal conductivity of molten SnS is in the same range is suggested by Glazov et al.³⁶, assuming molten sulfides share similar chain- and/or ring-like structure. However extreme caution shall be used when applying such analogy to quantitative analysis since its validity depends on a precise description of ordering and structure in molten materials, which is mostly unknown.

1.2 Radiative thermal conduction

Conventional radiative exchange between two surfaces based on Stefan-Boltzmann law does not depend on the media if it is *transparent* to radiation, such as vacuum. At the other extreme when the media is completely opaque to radiation, such as a metal, there is no radiative exchange between the two surfaces. All heat is transferred by conduction if the metal is solid. For a semiconductor that is partially transparent, radiation can slightly penetrate into the bulk of the material due to its finite absorption. The result is that radiation can now be transferred through slices of the semiconductor material in a conductive manner, in contrast to more conventional radiative heat transfer. Such heat transfer mechanism is called *radiative thermal conduction* and has been proposed by Schuster in 1903.³⁷

Radiative heat transfer can be estimated from the emissivity/absorption of photons by the material in the wavelengths of relevance for radiation at the temperature of interest. As show for Si by Sato,³⁸ three fundamental mechanisms are at play for solid semiconductors: 1) band-to-band transition, 2) free-carrier interaction, and 3) lattice vibration. According to Sato, the emission of photons with wavelength below the band-gap is due to band-to-band transition. The emission in the near-infrared wavelength range (above the band-gap) is caused by free-carrier interaction with photons. As temperature increases, more electrons from the valence band are thermally excited to the conduction band, becoming free charge carriers. For solid Si, spikes in absorption at wavelengths higher than 6 μm are found related to lattice vibrations. This later contribution is less relevant in the case of molten semiconductors since there is no lattice structure in liquids.

Radiative thermal conductivity (κ_{rad}) can be defined following equation (2) where n is the refractive index, α is the absorption coefficient, and τ is the Stefan-Boltzmann constant.

$$\kappa_{rad} = \frac{16n^2\tau T^3}{3\alpha} \quad (2)$$

If the optical properties of refractive index and absorption coefficient for a semiconductor are known, its radiative thermal conductivity can be evaluated. We were not able to find such report for molten semiconductors in the prior literature.

1.3 Natural convection

Convection, more specifically natural convection for a fluid in absence of external agitation is here considered buoyancy-driven. It has been extensively studied both theoretically and experimentally. Often, a temperature gradient under gravity is present, i.e. liquids heated from a bottom horizontal plate. Some pioneer works^{39–44} provided qualitative descriptions of both heat and mass transfer under

such conditions, where liquid motion is not smooth and tranquil. Instead characteristic time periods are observed during which local velocity and temperature disturbances are clearly observed. In heat transfer, those are described as "*thermals*" - packets of heated liquid that abruptly leave the heated surface. Accompanying thermals creation is an observed change of the hot surface temperature. In steady-state, departure and creation of thermals are alternating and an oscillatory temperature variation is observed. This phenomenological observation is often used to evidence natural convection. Quantitative studies⁴⁵⁻⁵⁸ have been performed for specific geometries and temperature boundary conditions (e.g. symmetric vs. asymmetric heating). Those provide relationship between dimensionless numbers representing the extent of convective and conductive transfer. A dimensionless transport number provides the effective convective conductivity for thermal or mass transfer. Regardless of this literature database, not much research had been devoted to heat transfer by natural convection specifically for high temperature molten semiconductors.

Prior art is available for liquid metals⁵⁹⁻⁶³ suggesting natural convection leads to an effective thermal conductivity that is 7 to 10 times the intrinsic thermal conductivity of the liquid metal. Similar conclusion is drawn for non-metals although the data are more limited. For example, molten InSb studied under microgravity suggests enhancement by a factor 2 to 3.⁶⁴ The closest study to molten SnS is by Williams et al. with molten AgS⁶⁵ in the same concentric cylinder cell geometry as investigated herein.¹ Williams et al. measure the total apparent thermal conductivity of molten AgS while varying the radius of the concentric cylinder. Based on the resultant linear relationship, it is concluded that natural convection amounts to around $0.4 \text{ W m}^{-1} \text{ K}^{-1}$, nearly 35% of the total apparent thermal conductivity ($\approx 1.2 \text{ W m}^{-1} \text{ K}^{-1}$), and that radiative thermal conduction is negligible.

Although accurate data on physical and thermal properties of molten SnS are not readily available, estimates can be used to calculate the Rayleigh number Ra_L for the geometry of interest,

$$Ra_L = \frac{g\beta\Delta TL^3}{\delta\nu} \quad (3)$$

Where g is the gravitational acceleration, β is the volumetric coefficient of thermal expansion, ΔT is the temperature difference, L is the characteristic length (here 5.1 mm), δ is the thermal diffusivity and ν is the kinematic viscosity. Table 1 below shows the properties^{66,67} estimated for SnS at 940°C, leading to a Rayleigh number of 1.44×10^4 , indicative that the natural convection liquid flow is laminar ($10^4 < Ra_L < 10^9$). This suggests that convection is not insignificant. The Nusselt number (Nu_L) is then used to evaluate the effective thermal conductivity due to natural convection (hL), expressed as following

$$Nu_L = \frac{hL}{\kappa} \quad (4)$$

The Nusselt number represents the ratio of convective heat transfer (hL) to conductive heat transfer (κ). The empirical correlation between Rayleigh and Nusselt numbers for concentric cylinder geometry is given by the following equation^{68,69}

$$Nu_L = 0.133Ra_L^{0.33}(H/L)^{-0.32} \quad (5)$$

where H/L is the aspect ratio of the annulus between the concentric cylinder.

Density (ρ), kg m ⁻³	Volumetric thermal expansion (β), K ⁻¹	Heat capacity (C_p), J kg ⁻¹ K ⁻¹	Thermal conductivity (κ), W m ⁻¹ K ⁻¹	Thermal diffusivity (δ), m ² s ⁻¹
4.282 x 10 ³	1.59 x 10 ⁻⁴	4.97 x 10 ²	1 to 2	9.4 x 10 ⁻⁷
Dynamic viscosity (μ), Pa s	Kinematic viscosity (ν), m ² s ⁻¹	Aspect ratio (H/L)	Prandtl number (Pr)	Nusselt Rayleigh number (Ra_L)
3.4 x 10 ⁻³	7.94 x 10 ⁻⁷	6.1	0.844	1.44 x 10 ⁴

Table 1. Properties of SnS at 940°C used to evaluate the extent of natural convection, along with characteristic dimensions of the studied geometry

The conclusion of Williams et al. for molten AgS and our preliminary calculations suggest the need to experimentally measure the total apparent thermal conductivity of molten SnS. We herein report such measurements with 3 methods. First, we use a thermal model that reproduces the experimental temperature difference measured across the melt. Second, we provide an estimate based on the thermopower performance of the cell. Third, we estimate the share of thermal conductivity due to natural convection using the results of the non-dimensional fluid mechanics calculation.

2. Experimental

Tin sulfide (SnS) synthesis procedure is described in reference 1. The solid material exhibits no noticeable contamination or off-stoichiometry as analyzed with X-ray diffraction of its powder or Electron Dispersive X-ray analysis of its cross section after solidification in an electron microscope. The electrode and container is graphite, a material that is chemically and mechanically stable in presence of liquid sulfides. The apparent thermal conductivity of the SnS melt can be estimated from the electrical conductivity reported by Boutin and Bourgon⁷⁰ and the Figure of Merit and Seebeck coefficient reported in our prior work.¹ The Figure of Merit is back calculated from the experimental thermoelectric efficiency (η_{exp}) from the following equations:

$$\eta_{exp} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + z\bar{T}} - 1}{\sqrt{1 + z\bar{T}} + \frac{T_C}{T_H}} \quad (6. a)$$

$$z\bar{T} = \frac{s^2 \sigma}{\kappa} T \quad (6. b)$$

where T_H is the hot-side temperature, T_C is the cold-side temperature, $z\bar{T}$ is the figure of merit at the average temperature $\bar{T}$, s is the Seebeck coefficient, σ is the electrical conductivity.

The experimental thermoelectric efficiency is obtained by comparing the power generated by the melt (P_{out} which excludes contributions from graphite, nickel and copper as explained and reported in reference 1) with the input heat flowing through the melt in the following equation,

$$\eta_{exp} = \frac{P_{out}}{0.4 Q_{Heating}} \quad (7)$$

where $Q_{Heating}$ is the total heating element power input. The factor 0.4 is the ratio of the height of the molten material to that of the hot zone of the heating element. This factor represents the fact that 40% of the total heat generated by the heating element goes through the molten material in the concentric, axisymmetric configuration of the device.

3. Modeling.

A computer model of the thermoelectric test cell was built to simulate the steady-state temperature difference across the melt. The model reproduces the key device dimensions schematically shown in Figure 1 and all the components of the experimental cell, using the actual materials which thermal properties values are found in the literature (e.g. insulation blanket, graphite cylinder, electrode leads etc.).⁷¹⁻⁷⁶

The steady-state heat transfer equations were solved in 3 dimensions using finite elements analysis with Heat Transfer Physics, in the module Heat Transfer of COMSOL Multiphysics (version 4.2). The module solves Equation 8.a. The first thermal boundary condition used herein is the silicon carbide element heating power ($Q_{Heating}$ in Equation 8.b) normalized by the element hot-zone outer area A (hot-zone height of 76.2mm, radius of 5mm). This heat is allowed to radiate through the inner gap toward the graphite inner wall using the emissivity (E_i) of graphite and silicon carbide, and the corresponding geometric area of the radiating surface (A_i) and view factor (F_i) as shown with equation 8c. The remaining heat transfer through the inner graphite wall, liquid SnS, the outer graphite wall and the thermal insulations is modeled as conduction using equivalent thermal conductivity as shown in equation 8d. The heat transfer on the outermost shell toward the test cell atmosphere is modeled as natural convection with a fixed average heat-transfer coefficient ($h = 25 \text{ W m}^{-2} \text{ K}^{-1}$) and the second boundary condition, the ambient temperature T_∞ (Equation 8.e):

$$\frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\kappa \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right) = 0 \quad (8. a)$$

$$q_{in} = \frac{Q_{Heating}}{A} \quad (8. b)$$

$$q_{rad} = \sigma E_i A_i F_i (T_i^4 - T_{i+1}^4) \quad (8. c)$$

$$q_{conduction} = -\kappa_{cond} \nabla T \quad (8. d)$$

$$q_{convection} = h(T_{Shell} - T_\infty) \quad (8. e)$$

The model assumed the molten material was opaque to radiative heat transfer. Convection and radiative thermal conduction within the melt are therefore modeled as part of an overall, apparent thermal conductivity. The apparent conductivity simulated from such model has therefore two contributions: 1) SnS intrinsic thermal conduction and 2) convection and radiative thermal conduction, each with an effective thermal conductivity.

The model confirmed what was found experimentally by temperature measurement; there is negligible spatial variation of the inner or the outer surface temperature of molten SnS. This is observed because the liquid is in direct contact with the graphite wall and the heater is longer than the height of the liquid annulus. Varying apparent thermal conductivities for the SnS melt were input into the model to reproduce the temperature difference with the fixed boundary conditions described above. The apparent conductivity value that allows best replication of all the experimentally measured temperatures was selected as the total apparent thermal conductivity of the thermoelectric melt. For example, the experimental temperature difference measured across the SnS melt was around 50°C. A series of simulations were performed with input SnS thermal conductivity from 1-10 $\text{W m}^{-1} \text{ K}^{-1}$. The input

thermal conductivity that allowed the model to output a simulated temperature difference of 50°C was then selected as the total apparent thermal conductivity of the thermoelectric SnS melt. It was found that the simulated temperature difference was only sensitive to the input thermal conductivity for a given heating power $Q_{Heating}$. It was nearly unaffected by other parameters such as the thermal conductivity of the insulation or the convection heat transfer coefficient at the outermost shell.

4. Results

Figure 2 shows the simulated apparent thermal conductivity, evaluated from the thermal model for each experimental heating element power input, represented by a single average temperature. The total apparent thermal conductivity derived from SnS experimental power conversion and its electrical properties, based on Equation 6.a and 6.b, is presented in Figure 2 for comparison. The simulated apparent thermal conductivities are in good agreement with the values calculated from experimental thermoelectric efficiency and the melt electrical properties. Such apparent thermal conductivity represents the sum of all possible heat transfer mechanisms present within the molten SnS sample in the conditions of the thermoelectric test cell experiments. The apparent thermal conductivity is increasing with temperature from SnS melting up to around 1000°C, above which the rate of increase decreases indicating a possible plateau in total heat transfer.

Figure 2 Temperature variation of the experimental apparent thermal conductivity (red squares) and the simulated apparent thermal conductivity (black dots). The shaded region represents the expected intrinsic thermal conductivity for molten sulfides.

The dashed line represents the electronic contribution to thermal conductivity based on Wiedemann-Franz law (i.e. a metal) for the fixed Lorentz number.

The shaded region in Figure 2 represents the expected intrinsic thermal conductivity for molten sulfides based on a compilation of data for different molten sulfide systems known to date.^{6,33,77} Such conductivity is anticipated to be mostly molecular and electronic. It is clearly 3 to 4 times lower than the apparent conductivity measured experimentally. The dashed line represents the electronic thermal conductivity calculated based Wiedemann-Franz law assuming the universal Lorentz number of $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, as an illustration of the anticipated behavior of a metallic system at such temperature. The uncertainty in this later number does not affect the key conclusion that the thermal conductivity for our study is not solely electronic.

4.1 Radiative thermal conductivity:

The temperature of operation of SnS in the thermoelectric test cell ranges from 900 to 1050°C. In this temperature range, a black body emits most photons with wavelength from 2.19 to 2.47 μm based on Wien's Displacement law. Therefore, it is of most interest to estimate radiative thermal conductivity in this near-infrared range.

Based on the work of Sato on silicon,³⁸ absorption in near-IR range is mostly due to free charge-carrier interaction with photons, as quantified by Vandenabeele and Maex.⁷⁸ As a first approximation, and since SnS and solid silicon have similar band gaps around 1.1-1.2 eV,⁷⁹ it is assumed that the absorption behavior of molten SnS as a function of temperature and incoming photon wavelength can be described by the same equation developed by Vandenabeele and Maex.

The refractive index of a material increases slightly with temperature, with a temperature coefficient usually below 10^{-4} K^{-1} in the near-IR wavelength range.⁸⁰⁻⁸⁴ At around 2-2.5 μm , refractive index of solid SnS stays roughly constant at 2.5-4.5 depending on the synthesis techniques.⁸⁵⁻⁹¹ Taking into account the difference in temperature between solid and molten SnS, a maximum value of 4.6 is used as a conservative estimate. Based on Equation 2, and the above-mentioned assumptions, we estimate the magnitude of radiative thermal conductivity to molten SnS next to its melting point to be no more than $0.33 \text{ W m}^{-1} \text{ K}^{-1}$, decreasing fairly rapidly with temperature.

4.2 Natural convection thermal conductivity

The Rayleigh number estimate from the introduction suggests that natural convection in molten SnS under a 50°C temperature gradient is not insignificant. As a qualitative evidence of the relatively high fluidity of molten SnS, direct observation under natural convection is provided in the supplementary video, in which molten SnS motion is captured in situ by a camera in a thermal imaging furnace. Figure 3 shows the total apparent thermal conductivity for concentric cylinder geometry using the properties of SnS of Table 1 and Equations 3 to 5. In absence of prior art, a key assumption is that the intrinsic thermal conductivity of molten SnS follows the temperature variation of the intrinsic thermal conductivity of molten Cu_2S ,^{6,8,35} shown as dashed line in Figure 3. The predicted apparent thermal conductivity by the fluid-dynamic model (blue line) agrees fairly well with the experimentally measured apparent thermal conductivity (red squares), especially for temperatures lower than 1000°C. However, a clear discrepancy is observed above around 1000°C.

Figure 3 Temperature variation of the experimental apparent thermal conductivity based on thermoelectric test cell (red squares) and predicted apparent thermal conductivity based on concentric cylinder fluid dynamics model (blue dots and plain line). The plain line is the predicted total apparent thermal conductivity due to both natural convection and intrinsic thermal conduction. The black dashed line represents the estimated intrinsic thermal conductivity of SnS estimated from molten Cu_2S data.

5. Discussion.

Thermal conductivity from natural convection based on Nusselt number calculation accounts for more than 60% (61 to 65%) of the total conductivity, indicating that natural convection is the major heat transfer mode for SnS in the conditions of reference 1. The close agreement presented in Figure 3 between the apparent thermal conductivity calculated from fluid dynamics and the experimental apparent thermal conductivity suggests a negligible contribution of radiative thermal conduction. This is qualitatively consistent with our expectation for a semi-transparent semiconductor. Additional studies of SnS with varying thickness would be of value, as a very thin sample is anticipated to exhibit limited radiative heat transfer and natural convection, leading to experimental data closer to the actual intrinsic conduction. Accurate measurements of the correspondingly small temperature difference for small thickness will however likely be challenging, as the thermal contact resistance at the electrode/melt may then be of similar order of magnitude.

Intrinsic thermal conduction is the second most important heat transfer mechanism. Clearly the accuracy of the intrinsic thermal conductivity used as input for fluid dynamics calculation is important because the calculated total apparent thermal conductivity is the sum of intrinsic thermal conduction and natural convection, both of which are dependent on the magnitude of intrinsic thermal conductivity. Although the Nusselt number will marginally be affected by errors in intrinsic thermal conductivity estimates, the absolute magnitude of the sum of intrinsic and natural convection heat transfer mechanisms will clearly be affected. Given the fact that the intrinsic thermal conductivity used for molten SnS is based on molten Cu₂S, further experimental quantification of molten SnS intrinsic thermal conductivity with the Laser Flash technique is warranted. Key challenges are likely 1) how to assure the heat transfer from the laser pulse to the liquid without excessive heat loss and 2) to find compatible crucible material for liquid containment while preventing corrosive vapor of molten SnS to damage the instrument.

One very intriguing observation from Figure 3 is that the apparent thermal conductivity from fluid dynamics calculation based on concentric cylinder geometry deviates from experimental measurements at around 1000°C. It is possible this is a true reflection of changes in intrinsic materials properties for SnS, a molten semiconductor at high temperature. Indeed, semiconductor-to-metal transition (or metallization), is expected as temperature is increased above melting for such liquid semiconductors.^{92,93} This is accompanied by a drastic change in electronic structure that shall be reflected by changes in materials properties such as density, heat capacity and viscosity, in particular on their temperature dependence.

Very limited studies on materials properties of molten semiconductors during metallization (e.g. Se_x-Te_{1-x}) have shown certain abnormal variation of density,⁹⁴ heat capacity,⁹⁵ thermal conductivity³⁴ at and around metallization temperature¹¹, all of which are important parameters for fluid dynamics calculation. Therefore, our study suggests that it is key to understand the effects of metallization on materials properties of molten semiconductors in order to better characterize their heat transfer properties.

6. Conclusions

This work provides for the first time a complete analysis of thermal transport in SnS, both intrinsically and in a given thermoelectric cell geometry. It reveals the good performance of the concentric cylinder geometry chosen for a first evaluation of thermopower generation, with agreement across 3 different means of evaluating the apparent thermal conductivity. Further analysis suggests the importance of natural convection in the overall heat-transfer, calling for evaluation of intrinsic thermal conductivity using a laser flash technique. The contribution from radiative heat transfer is suggested as minimal. The use of a cell geometry where both heat and mass transport properties are macroscopically affecting electrical and thermal signals with a molten semi-conductor may be beneficial to witness intrinsic changes in structure, e.g. metallization.

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