

The ideal thermal conductivity of single crystal α - and β - Si_3N_4

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The molecular dynamics method was used to simulate energy transport in α - and β - Si_3N_4 single crystals. The simulation data, in conjunction with the Green-Kubo formulation, was used to calculate the thermal conductivity of the single crystals, as a function of temperature. At a temperature of 300 K, it was estimated that the thermal conductivity (in units of $\text{W m}^{-1} \text{K}^{-1}$) in α - and β - Si_3N_4 , along the a - and c -directions, is approximately 105 and 225, and 170 and 450, respectively. The results were compared to existing experimental data and were found to be in reasonable agreement with existing results.

Keywords: Silicon nitride, Molecular dynamics, Thermal conductivity

1. INTRODUCTION

There are two crystal structures of silicon nitride, α - and β - Si_3N_4 , where the β configuration is the more stable of the two.¹ Both configurations exhibit slightly different mechanical and thermal properties that are not completely understood. Regardless of the difference between the two silicon nitride configurations, in order to understand, and thus control, the behavior of this type of ceramic at elevated temperatures some knowledge of the response of the material to temperature changes is required.

Microstructure is important in understanding the thermal conductivity of a ceramic since the phases present, and the distribution of the phases, all have a significant effect on heat transport. In addition, porosity, grain boundaries and structural defects (e.g. dislocations) are also important due to phonon, and photon, scattering. However, one factor that can not be ignored is the effect of temperature on thermal conductivity. In general, increased temperatures result in increased lattice vibrations, which result in increased phonon scattering. In particular, in Si_3N_4 ceramics only acoustic phonons contribute significantly to heat transport.

In this study, the ideal thermal conductivity of α - and β - Si_3N_4 single crystals was determined. Furthermore, the dependence of the thermal conductivity as a function of temperature was calculated. The calculations were performed using a molecular dynamics method, in conjunction with the Green-Kubo formulation. In the present paper, initially the simulation method will be outlined including the procedure employed to calculate the thermal conductivity from the molecular dynamics data. Following this, the results of the simulation procedure will be presented with a detailed discussion.

2. THERMAL CONDUCTIVITY

2.1 The molecular dynamics method

The molecular dynamics technique, which in this case also incorporates the Green-Kubo method (discussed in the following section), has been employed successfully in the past to investigate the thermal properties of silicon crystals,² KCl,³ and diamond.⁴ In the case of Si_3N_4 , lattice vibrations are assumed to govern energy transport, which are modeled on pre-defined potential functions. The total potential energy, for Si_3N_4 structures, of the system (E_T) was defined as the sum of 2-body ($E_{ij}^{(2)}(r_{ij})$) and 3-body ($E_{ijk}^{(3)}(r_{ij}, r_{ik}, \theta_{jik})$) interactions as proposed by Vashishta *et al.*,⁵

$$E_T = \sum_{i < j} E_{ij}^{(2)}(r_{ij}) + \sum_{i, j < k} E_{ijk}^{(3)}(r_{ij}, r_{ik}, \theta_{jik}), \quad (1)$$

where i, j and k refer to atoms in the system, r_{ij} is the length of the ij bond, and θ_{jik} is the bond angle between the ij and ik bonds. The 2-body and 3-body energy terms are given as,

$$E_{ij}^{(2)}(r_{ij}) = A_{ij} \left\{ \left(\frac{\sigma_i + \sigma_j}{r_{ij}} \right)^{\eta_{ij}} + \frac{Z_i Z_j}{r_{ij}} e^{\left(-\frac{r_{ij}}{r_{s1}} \right)} - \frac{\alpha_i Z_j^2 + \alpha_j Z_i^2}{2r_{ij}^4} e^{\left(-\frac{r_{ij}}{r_{s4}} \right)} \right\}, \quad (2)$$

$$E_{jik}^{(3)}(r_{ij}, r_{ik}, \theta_{jik}) = \left. B_{jik} e^{\left(\frac{l}{r_{ij}-r_c} + \frac{l}{r_{ik}-r_c} \right) \left[\cos \theta_{jik} - \cos \theta_{jik}^0 \right]} \right\} \quad (3)$$

where $A, \sigma, \eta, Z, r_{st}, \alpha, r_{s4}, B, l, r_c, \theta^0$ are parameters, determined for Si₃N₄ by Vashishta *et al.*⁵

The 2-body potential function consists of steric repulsion, Coulomb interaction, and dipole interaction through electronic polarization. The 3-body function involves bond-bending terms, to take into account covalent bonding. This latter potential has been applied to various molecular dynamics calculations and has resulted in excellent predictions of equilibrium lattice parameters, elastic constants, phonon densities of states, and specific heat data.^{5,6,7,8} It has been shown previously that it is important to take into account quantum corrections for low-temperature molecular dynamics simulations of the thermal conductivity.⁹ Nevertheless, this effect is only significant for temperatures below approximately 300 K.⁹ Hence, in this study the thermal conductivity is only calculated for temperatures equal to, or greater than, 300 K.

2.2 The Green-Kubo method

Although, the molecular dynamics method can be used to characterize energy transport, no direct information of the thermal conductivity can be obtained. Instead, the thermal conductivity, κ , is calculated using the Green-Kubo¹⁰ method, which is based on the evaluation of the decay of equilibrium fluctuations of the heat flux vector, $S(t)$, of the simulated system. The heat flux vector¹¹ for a system of atoms is defined as,

$$S(t) = \left. \begin{aligned} & \frac{d}{dt} \sum_i r_i \tilde{E}_i \\ & = \sum_i v_i \tilde{E}_i + \sum_{i,j,i \neq j} (F_{ij} \cdot v_i) r_{ij} \end{aligned} \right\} \quad (4)$$

where v_i is the velocity of atom i , v_{ij} and r_{ij} represent the force acting on atom i due to atom j and the directional vector from atom i to atom j (where $r_{ij} = r_i - r_j$), respectively, and \tilde{E}_i is the excess amount of site energy

at atom i . In equation (4) the first term, $\sum_i v_i \tilde{E}_i$, is a

convection term that describes atomic diffusion, and contributes significantly only at high temperatures. The

second term, $\sum_{i,j,i \neq j} (F_{ij} \cdot v_i) r_{ij}$, represents the correlation between neighboring atoms and includes anharmonic effects.⁹ All of the quantities in equation (4) can be determined directly from the molecular dynamics simulation results. Additionally, \tilde{E}_i can be obtained from the following relation (the sum of the 2- and 3-body terms of the potential and kinematics energy),

$$\tilde{E}_i = \left. \begin{aligned} & \sum_{j,i \neq j} E_{ij}^{(2)}(r_{ij}) + \\ & \sum_{j,k,i \neq j,k,j > k} E_{jik}^{(3)}(r_{ij}, r_{ik}, \theta_{jik}) + \frac{1}{2} m_i |v_i|^2 \end{aligned} \right\} \quad (5)$$

where $E_{ij}^{(2)}$ and $E_{jik}^{(3)}$ are defined in equation (2) and (3), respectively, and m_i is the mass of atom i . Thus, the directional thermal conductivity can be related directly to the time correlation function of the heat flux vector using the relation,

$$\kappa_x(T) = \frac{1}{k_B V T^2} \int_0^\infty \langle S_x(0) S_x(t) \rangle dt \quad (6)$$

where S_x is the heat flux vector along the x -direction (and the relation is the same in the y - and z - directions), V the volume of the system, T the temperature of the system and k_B is Boltzmann's constant.⁹ In this study, a direct method is employed to estimate the time correlation function in equation (6).

The direct method of estimating the time correlation function of the heat flux vector was performed using a *double averaging method*. The ensemble, represented by the heat flux vector, was divided into sub-ensembles for a given initial value. For example, in the case of the thermal conductivity in the x -direction (given by equation (6)), $S_x(0) = S_x(\tau_0)$, and a final value $S_x(\tau_0 + \tau)$, which represents many microscopic states with a given macroscopic value, $S_x(0)$. The time-average of each individual sub-ensemble was calculated, and then the average over all sub-ensembles was determined, to obtain the time correlation function. Using the time-average of the sub-ensemble, in a discretized form, the non-normalized correlation function in the x -direction can be written as,

$$\langle S_x(0) S_x(t) \rangle = \frac{1}{\tau_{\max}} \sum_{\tau_0=1}^{\tau_{\max}} S_x(\tau_0) S_x(\tau_0 + \tau) \quad (7)$$

where the average is over τ_{\max} time origins, which is the total number of sub-ensembles. Clearly, in this case, for each value of τ_0 , the value of $\tau_0 + \tau$ must not exceed the maximum simulation time. More importantly, if the time step τ were too large the statistics of this long time would be poor, since there would exist few terms in the summation of equation (7). In general, the time correlation function should decay to zero in a time that is short compared to the total simulation time, and thus only a short time (equivalent to a few hundred data points) is of interest. Furthermore, for a short time, τ , the correlation function can be determined with greater statistical accuracy because the total number of sub-ensembles in the average would be greater. The time origin of each sub-ensemble should not be defined such that they are successive data points, even though this is suggested in the definition of equation (7). Instead, the summation should be determined for time origins that

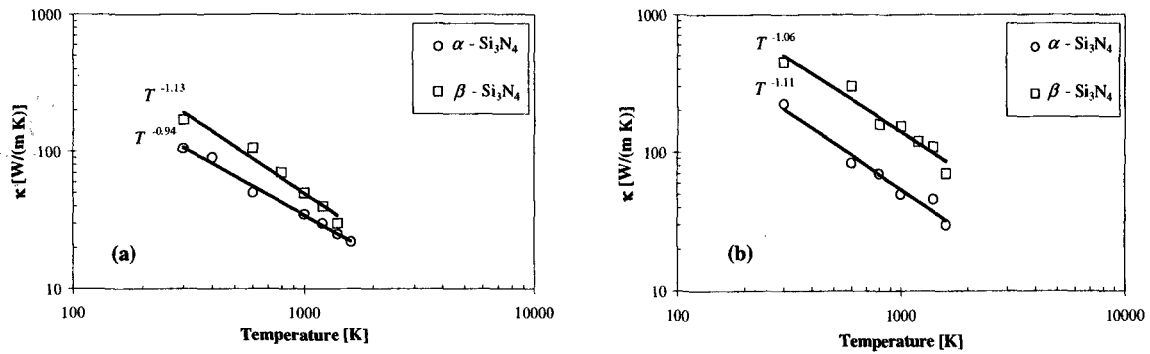


Figure 1. Plot of the thermal conductivity as a function of temperature, for the α - and β - Si_3N_4 single crystals, in the (a) a - and (b) c -axial directions.

are sufficiently distant in time. This is the case since successive origins in time would be highly correlated.

3. MOLECULAR DYNAMICS SIMULATION RESULTS

The supercell dimension, in the direction of the heat flux calculation, has a significant effect on the accuracy of the estimated thermal conductivity and on the computation time. It was necessary, therefore, to estimate an optimum supercell size. The thermal conductivity was calculated for various supercell lengths in the a - and c -directions, at a constant temperature of 300 K. From the data it was estimated that the optimum characteristic length in the a -direction is ~ 4.7 nm and in the c -direction is ~ 3.5 nm. Thus, the unit cell of the α - Si_3N_4 single crystal for the simulation contained, 12 silicon atoms and 14 nitrogen atoms. Correspondingly, the β - Si_3N_4 single crystal unit cell contained, 6 silicon atoms and 8 nitrogen atoms. The typical supercell employed in this study contained 672 atoms, constructed from a predefined number of unit cells. The relevant structural data of the α - and β - Si_3N_4 single crystals supercells are summarized in Table I. Periodic boundary conditions were imposed along each direction of the supercell, to ensure energy (and momentum) conservation while allowing energy to flow through the boundaries.

Initially, for a predefined temperature, constant volume and constant number of atoms, the atomic configuration (of the supercell) was relaxed to equilibrium, (a force-free mechanically stable configuration) over a period of approximately 12 ps. After equilibration, the molecular dynamics simulation was carried out for approximately 3.5 ns, during which the heat flux vector, S , was calculated (at constant volume, constant total system energy and constant number of atoms) approximately every 1.2 fs. The thermal conductivity was calculated using the double averaging method for an averaging time of approximately 12 ps. This averaging time, over the total simulation time of 3000 ps, is equivalent to approximately 250 sub-ensembles. The thermal conductivity was then calculated by averaging the sub-ensemble results, over all the sub-ensembles. The data of the thermal conductivity, for the α - and β - Si_3N_4 single crystals, as a function of temperature, in the a - and c -

directions are presented in figures 1(a) and (b), respectively.

Table I. Relevant structural data for the α - and β - Si_3N_4 single crystal supercells, employed in the molecular dynamics simulation procedure.

(a) α - Si_3N_4	
Number of atoms	672
Optimum Supercell Dimensions (nm)	a -direction: $x = 4.7, y = 1.4, z = 1.7$ c -direction: $x = 1.6, y = 1.4, z = 3.4$
Lattice Constants (nm)	$a = 0.7818, c = 0.5591$

(b) β - Si_3N_4	
Number of atoms	672
Optimum Supercell Dimensions (nm)	a -direction: $x = 4.6, y = 1.3, z = 1.7$ c -direction: $x = 1.7, y = 1.3, z = 3.5$
Lattice Constants (nm)	$a = 0.7595, c = 0.2902$

4. DISCUSSION

The thermal conductivity as a function of temperature, obtained from the molecular dynamics procedure, is presented in figure 1. For the β - Si_3N_4 single crystal the thermal conductivity of the material at 300 K has been measured experimentally:¹² 69 and 180 [W/(m K)] in a - and c - directions respectively. At present, however, there are no reported experimental data of the thermal conductivity of a α - Si_3N_4 single crystal. In the case of the β - Si_3N_4 single crystal the lower experimental result was expected. The current results were calculated for a crystal structure with no impurities or structural defects. The 'real' β - Si_3N_4 single crystal does contain structural anomalies and impurities and, thus, results in an increase in phonon scattering, resulting in a lower thermal conductivity. In figure 1, the functional dependence of the simulated thermal conductivity to temperature is also shown. The dependence was estimated by calculating a power function of best fit to the data. It is reasonable to argue that the 'real' material thermal conductivity would be expected to exhibit a functional dependence with respect to temperature as T^{-1} .¹³ Clearly, within

calculation error, the current data exhibits a behavior that is in good agreement with the T^{-1} behavior.

In this study, the phonon mean free path in the crystals examined can be in the order of tens of nanometers. Thus, it is reasonable to expect that for accurate results the characteristic supercell dimension should be as large, if not larger, than the phonon mean free path. The phonon mean free path can be calculated using the thermal conductivity equation obtained from the kinetic theory of gases,¹⁴ $\kappa = (1/3)v_p C < l_p >$, where v_p is the phonon velocity, C is the heat capacity and $< l_p >$ is the phonon mean free path. Using available data it was determined that a typical phonon mean free path is in the order of ~ 20 nm, at 300 K. This result is much larger than the optimum supercell size. When the supercell size is small, there is the possibility of a periodically equivalent phonon travelling through the supercell, and returning to the phonon point of origin. However, it is possible to obtain accurate thermal conductivity results for a characteristic supercell dimension much smaller than the phonon mean free path.⁴ This is the case since in the method employed in this study the energy current correlation time is much shorter than the energy relaxation time. A rigorous proof is not given here as a matter of brevity, however, Che *et al*⁴ and, Volz and Chen² provide a detailed analysis.

The molecular dynamics results also show that the thermal conductivity of the β -phase is higher than the α -phase. This maybe the case since the β -Si₃N₄ single crystal has only half as many atoms per unit cell. Workers have reported that the relation between the thermal conductivity and coordination number is $\kappa \propto n^{-2/3}$, however, the relations $\kappa \propto n^{-1/3}$, and $\kappa \propto n^{-1/2}$ have also been reported in the literature.¹⁵ From the simulation results it is found that $\kappa \propto n^{-1 \pm 0.5}$. The dependence of the thermal conductivity on the number of atoms per unit cell is a point of contention, which requires further investigation. However, it has been shown by an extensive study¹⁶ that, although the tetrahedral atomic structure is favorable for a high thermal conductivity, a higher coordination number does result in a lower thermal conductivity.

It is clear that the silicon nitride ceramics are a class of materials that exhibit excellent thermal conductivity. However, the current investigation has not attempted to determine the effects of impurities and structural defects on the thermal conductivity. In order to ascertain such effects, it is suggested that the molecular dynamics calculation be employed to investigate atomic configurations that have such anomalies introduced into the crystal structure. The ability to introduce specific atomic impurities at specific atomic lattice locations, also the case when looking at the effect of structural defects would be of significant advantage. It is already well known that such anomalies significantly affect thermal properties of a solid. It is the future purpose of the current authors to investigate such effects using the molecular dynamics procedure. It is expected that such a study would result in a greater understanding of the mechanisms of heat transport in solids.

5. CONCLUSION

In this study, the molecular dynamics method was used to simulate energy transport in α - and β -Si₃N₄ single crystals. Using the simulation data, the Green-Kubo formulation was applied to calculate the thermal conductivity of the single crystals, as a function of temperature. At a temperature of 300 K, it was determined that the thermal conductivity (in units of W m⁻¹ K⁻¹) in α -Si₃N₄ and β -Si₃N₄, along the a - and c -directions, is approximately 105 and 225, and 170 and 450, respectively. It is clear from comparisons with existing experimental data that the molecular dynamics calculation is in reasonable agreement. Furthermore, it is clear that a higher thermal conductivity for 'real' silicon nitride specimens could be obtained, if the existing methods for producing the ceramics could be refined to result in fewer structural defects and impurities.

6. ACKNOWLEDGEMENTS

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- ¹ R. Grün, Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **35**, 800 (1979).
- ² S. G. Volz and G. Chen, Phys. Rev. B **61**, 2651 (2000).
- ³ G. V. Paolini, P. J. D. Lindan, and J. H. Harding, J. Chem. Phys. **106**, 3681 (1997).
- ⁴ J. Che, T. Çağın, W. Deng, and W. A. Goddard III, J. Chem. Phys. **113**, 6888 (2000).
- ⁵ R. Vashishta, R. K. Kalia, A. Nakano, and I. Ebbsjö in: M. F. Thorpe and M. I. Mitkova (Eds.), Amorphous Insulators and Semiconductors, Kluwer, Dordrecht, 1996, p. 151.
- ⁶ C. K. Loong, P. Vashishta, R.K. Kalia, and Ebbsjö, Europhys. Lett. **31**, 201 (1995).
- ⁷ A. Nakano, R.K. Kalia, and P. Vashishta, Phys. Rev. Lett. **75**, 3138 (1995).
- ⁸ K. Tsuruta, A. Nakano, R.K. Kalia, and P. Vashishta, J. Am. Ceram. Soc. **81**, 433 (1998).
- ⁹ Y. H. Lee, R. Biswas, C. M. Soukoulis, C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **43**, 6573 (1991).
- ¹⁰ H. Kitagawa, Y. Shibutani, and S. Ogata, Modelling Simul. Mater. Sci. Eng. **3** 521 (1995).
- ¹¹ R. W. Zwanzig, Annu. Rev. Phys. Chem. **16**, 67 (1965).
- ¹² Bincheng Li, L. Pottier, J. P. Roger, D. Fournier, K. Watari and K. Hirao, J. Euro. Ceram. Soc. **19**, 1631 (1999).
- ¹³ K. Watari, J. Ceram. Soc. Japan **109**, 1 S7 (2001).
- ¹⁴ C. Kittel, *Introduction to Solid State Physics*, 5th Edition (John Wiley & Sons, Inc., New York, 1970), p.186.
- ¹⁵ M. Roufosse and P. G. Klemens, Phys. Rev. B **7**, 5379 (1973).
- ¹⁶ D. P. Spitzer, J. Phys. Chem. Solids **31**, 19 (1970).

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