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The temperature dependence of the Young's modulus of $MgSiN_2$, AlN and Si_3N_4

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Abstract

The temperature dependence of the Young's modulus of $MgSiN_2$ and AlN was measured between 293 and 973 K using the impulse excitation method and compared with literature data reported for Si_3N_4. The data could be fitted with $E = E_0 - B \cdot T \exp(-T_0/T)$. The values of the fitting parameters E_0 and T_0 are related to the Debye temperature, and the parameter B to the harmonic character of the bond.

Keywords: AlN; Debye temperature; Elastic modulus; $MgSiN_2$; Si_3N_4

1. Introduction

The relatively new ternary adamantine type compound $MgSiN_2$, which can be deduced from the well known AlN by replacing two Al^{3+} ions by one Mg^{2+} and one Si^{4+} ion, might be interesting for specific applications because of its favourable chemical, mechanical and thermal properties.[1–8]

We pointed out[6] that in order to understand the (thermal) properties of $MgSiN_2$, AlN and other (new) potentially interesting materials more insight is needed into the parameters that determine the intrinsic thermal conductivity. Two important parameters that determine the intrinsic thermal conductivity are the Debye temperature θ (K) and Grüneisen parameter γ (−).[6,9–12] The Debye temperature can be evaluated from elastic constants E (Young's modulus) [Pa] and ν (Poisson's ratio) (−).[13] For evaluation of the Grüneisen parameter elastic constants as a function of the temperature are needed. So far, only room temperature values for the elastic constants have been published ($MgSiN_2$: $E = 235$ GPa and $\nu = 0.232$ [2] and AlN: $E = 308-315$ GPa and $\nu = 0.179-0.245$[14–16]).

In this paper we report the Young's modulus of $MgSiN_2$ and AlN as a function of the temperature between 293 and 973 K. The temperature dependence of the Young's modulus was described with the empirical expression $E = E_0 - B \cdot T \exp(-T_0/T)$ which was previously shown to be valid by Wachtman for several oxides.[17] Also temperature dependent Young's modulus data for the related nitride compound Si_3N_4[18] were fitted using this expression. For $MgSiN_2$, AlN and Si_3N_4 the fitting parameter E_0 was used for calculating the Debye temperature θ_0. The values obtained for B and T_0 from fitting of the experimental data are discussed in view of the analytical expressions of Anderson.[19]

2. Experimental section

The preparation of the $MgSiN_2$ ceramic disks (ø 33×3 mm) with hot-pressing (1550–1650°C, 75 MPa, N_2 atmosphere, 2 h) is described elsewhere.[5,8,20] Three fully dense ($\rho = 3.14-3.15$ g cm^{-3}) samples (RB10, RB31 and RB33) processed in somewhat different ways, were selected to measure the temperature dependence of the Young's modulus. X-ray diffraction (XRD) revealed that they contain some (<2 wt.%) α- and β-Si_3N_4 (RB10), MgO (RB31), and β-Si_3N_4 (RB33) as a secondary phase.[8] Clean grain boundaries were observed between the $MgSiN_2$ grains (~ 0.3–1.0 μm) with transmission electron microscopy (TEM). The AlN ceramics were obtained from Xycarb ceramics (Helmond, The Netherlands). The

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fully dense ($\rho = 3.29$ g cm^{-3}) AlN ceramic disk (ø 250 × 20 mm) was prepared by hot-pressing (1830°C, 35 MPa, N_2 atmosphere, 45 min) AlN powder (ART, grade A100) containing about 4 wt.% Y_2O_3 as an additive. The resulting ceramics contain some YAP ($YAlO_3$, JCPDS 33-41) and YAG ($Y_3Al_5O_{12}$, JCPDS 33–40) as detected with XRD, which are commonly found secondary phases for AlN sintered with Y_2O_3 addition. The grain size of the AlN ceramics was about 4 μm as observed on a fractured surface with a field emission scanning electron microscopy (FESEM).

For a fully dense $MgSiN_2$ disk (ø15×2.89 mm) the room temperature longitudinal v_l (m s^{-1}) and transverse sound velocity v_t (m s^{-1}) were measured at 10 and 20 MHz, respectively, using the pulse-echo method. From the sound velocities and the density ρ (kg m^{-3}) the room temperature Young's modulus E (Pa) and Poisson's ratio ν (−) were calculated using the formulas for isotropic materials:[21]

$$\nu = \frac{\left(\frac{v_l}{v_t}\right)^2 - 2}{2\left(\frac{v_l}{v_t}\right)^2 - 2}$$

$$E = 2v_t^2\,\rho(1+\nu) = v_l^2\rho\frac{(1+\nu)(1-2\nu)}{(1-\nu)}$$

The Young's modulus was measured from 293 to 973 K using the impulse excitation method[22] (GrindoSonic, Lemmens Elektronica BV, Belgium). For $MgSiN_2$ and AlN two different sample sizes of the same material were measured (rectangular bars l×b×h ~18×8×2 mm and ~18×5×2 mm). For comparison also some room temperature measurements on larger AlN bars (rectangular bars ~50×8×3 mm and ~50×6×3 mm) were performed. Each measurement was performed twice in order to obtain an impression of the accuracy of the data points and of the resulting fitting parameters.

The fundamental natural flexural frequency of the samples was measured every 5 K during heating and cooling. From this frequency, the sample dimensions and mass, the Young's modulus E [Pa] was evaluated using:[23,24]

$$E = 0.9465\frac{mf^2l^3}{bh^3}A$$

in which m (kg) is the sample mass, f (s^{-1}) the flexural frequency, l (m) the sample length, b (m) the sample width, h (m) the sample height and A a dimensionless shape factor dependent on sample length, sample width and Poisson's ratio. As the dependence of A on the Poisson's ratio is very limited, A can be approximated by: $A = 1 + 6.585(h/l)^2$.[24] The sample dimensions were corrected for thermal expansion in order to calculate the Young's modulus. The resolution of the flexural frequency measurement was 10 Hz for a typical resonance frequency of about 30 kHz.

For comparison temperature dependent literature data for Si_3N_4 (β-modification according to the processing temperature of 1750°C mentioned)[18] were taken for sample H-1 with 0.5 wt.% MgO addition. The Young's modulus data for this sample with the least amount of secondary phase were corrected for porosity [$E = E_{meas}/(2\rho_{meas}/\rho_{the} - 1)$][18] with ρ_{meas} (3.104 g cm^{-3}) and E_{meas} (varying between 302 and 291 GPa for temperatures between ~300 and ~1200 K, respectively) the experimental density and Young's modulus, respectively, and ρ_{the} (3.19 g cm^{-3}) the theoretical density of β-Si_3N_4.

The data obtained as a function of the absolute temperature were described using the empirical formula of Wachtman:[17]

$$E = E_0\text{-}B\cdot T\exp(\text{-}T_0/T)$$

in which E_0 [Pa] is the Young's modulus at 0 K, B (Pa K^{-1}) and T_0 (K) are fitting parameters.

3. Results and discussion

3.1. Evaluation of the measurements

For $MgSiN_2$ a longitudinal sound velocity of 10.17 ×10^3 m s^{-1} and transverse sound velocity of 5.90×10^3 m s^{-1} were measured. This resulted in a room temperature value for the Poisson's ratio ν of 0.246 and the Young's modulus E of 273 GPa. The Poisson's ratio is comparable with $\nu = 0.232$ given in the literature measured with the same pulse-echo technique.[2] The value of the Young's modulus reported before is considerably lower $E = 235$ GPa,[2] which may be (partially) ascribed to the lower density (98.9%) and purity (3.7 wt.% oxygen) of the sample described in the literature.[2]

For the impulse excitation experiments no hysteresis in the resonance frequency was observed during heating and cooling. The reproducibility of the measurements using the same sample was ±0.3 GPa (≈0.1%). The slight difference between the observed Young's moduli for the same material having different dimensions is caused by experimental errors in the sample dimension measurement, Δl, Δb and $\Delta h \approx 0.02$ mm leading to $\Delta E \approx 0.016E = 4.5$ GPa. Considering the experimental accuracy the Young's modulus at 293 K was the same for the various samples and equal about 279±4 and 312±4 GPa for $MgSiN_2$ and AlN, respectively. The room temperature value for $MgSiN_2$ is in good agreement with our value measured using the pulse-echo method (273 GPa), and our values for AlN (312 GPa) and Si_3N_4 (319 GPa) are in excellent agreement with

previously reported ones (AlN: 308–315 GPa[14–16] and Si_3N_4: 290–335 GPa)[25,26].

With increasing temperature the Young's modulus of $MgSiN_2$, AlN and Si_3N_4 slightly decreases (Fig. 1). As compared with the room temperature value the Young's modulus at 973 K for the $MgSiN_2$ samples has decreased with 12.6±0.2 GPa ($\Delta E/E_{293} = 0.045$), for the AlN samples with 12.9±0.2 GPa ($\Delta E/E_{293} = 0.041$) and for the Si_3N_4 sample with 8.3 GPa ($\Delta E/E_{293} = 0.026$). So, the temperature dependence of $MgSiN_2$ and AlN are similar whereas Si_3N_4 shows a smaller temperature dependence. As expected,[17] the temperature dependence of the experimental data is very well described by $E = E_0 - B \cdot T \exp(-T_0/T)$ (Fig. 1). As the Young's modulus shows no anomalies, this indicates that for all three materials the influence of microstructure and secondary phases on the temperature dependence of the Young's modulus can be assumed to be negligible. In Table 1 the values of the fitting parameters E_0, B and T_0 are presented. The average E_0 value for AlN of 314 GPa was calculated from the average observed E_{293} and the average values of B and T_0. Within the experimental accuracy the values of E_0, B and T_0 of the AlN samples are the same as all samples originate from one large homogeneous ceramic bar. Also for the several $MgSiN_2$ samples processed under somewhat different conditions (see Ref. 8) the values of E_0, B and T_0 are within the experimental error the same (see Table 1). A relatively large variation in T_0 is observed for the measurements performed on the same sample having the same size. For $T \geqslant T_0$ we can write for $E = E_0 - B \cdot T \exp(-T_0/T)$ $\approx E_0 - B \cdot T(1 - T_0/T) = (E_0 + B \cdot T_0) - B \cdot T$ resulting in a linear relation between E and T (as observed in Fig. 1) showing that the slope B can be easily evaluated whereas the constants E_0 and $B \cdot T_0$ are correlated. As $E_0 \gg B \cdot T_0$ the fitting parameter T_0 is relatively sensitive to small errors as compared to E_0 and B.

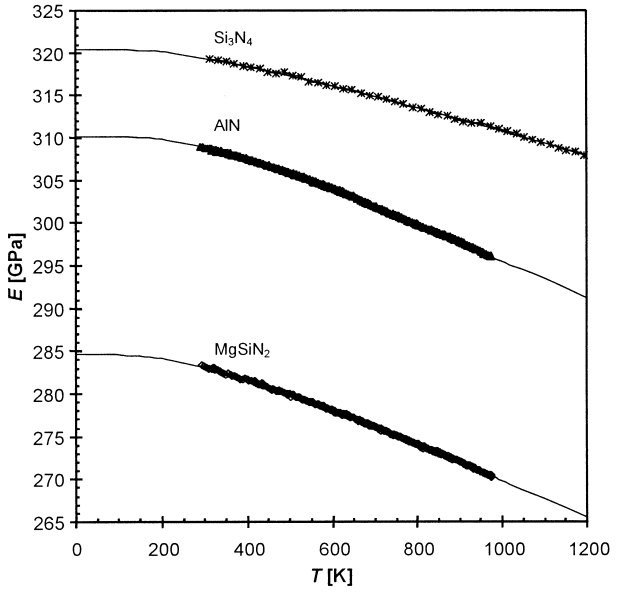

Fig. 1. A typical result obtained for the Young's modulus (E) as a function of the absolute temperature T between 293 and 973 K for a $MgSiN_2$ and AlN ceramic sample with fit $E = 284.8 - 0.0228 \cdot T \exp(-424/T)$ and $E = 310.2 - 0.0247 \cdot T \exp(-533/T)$, respectively. For comparison literature data for Si_3N_4[18] between 300 and 1200 K with fit $E = 320.4 - 0.0151 \cdot T \exp(-445/T)$ are included.

3.2. Interpretation of the fitting parameters

3.2.1. E_0

The average E_0 value (Young's modulus at 0 K) for $MgSiN_2$, AlN and Si_3N_4 was used to evaluate the Debye temperature at 0 K, θ_0 (K). The Debye temperature can be calculated from the average sound velocity (v_s (m s^{-1})) obtained from the longitudinal v_l (m s^{-1}) and transverse sound velocity v_t (m s^{-1}) using the elastic constants E and ν, and the density ρ (kg m^{-3}):[12,21,27]

$$v_l = \sqrt{\frac{E}{\rho}\frac{(1-\nu)}{(1+\nu)(1-2\nu)}}$$

$$v_t = \sqrt{\frac{E}{\rho}\frac{1}{2(1+\nu)}}$$

$$v_s = \left(\frac{1}{3}\left[\frac{1}{v_l^3} + \frac{2}{v_t^3}\right]\right)^{-\frac{1}{3}}$$

Subsequently the average sound velocity can be used to calculate the Debye temperature using:[12,13,27,28,29]

$$\theta = \frac{h v_s}{2k}\left(\frac{8s}{4\pi}\frac{N_A \rho}{M}\right)^{\frac{1}{3}}$$

in which h is Planck's constant (6.626×10^{-34} J s), k Boltzmann's constant (1.381×10^{-23} J K^{-1}), s (−) the number of atoms per formula unit, N_A Avogadro's number (6.023×10^{23} mol^{-1}) and M (kg mol^{-1}) the mol mass.

Using the Young's modulus and density at 0 K (E_0 and ρ_0, respectively) and the room temperature value of the Poisson's ratio ν, the Debye temperature θ_0 was calculated (see Table 2). The resulting Debye temperatures of all three compounds are in the same range (900–950 K) with $\theta_{MgSiN_2} = 900$ K, $\theta_{AlN} = 940$ K and $\theta_{Si_3N_4} = 955$ K. The values agree reasonably well with previously reported values for $MgSiN_2$, AlN and Si_3N_4 determined in different ways (see Table 3).

3.2.2. B and T_0

Anderson[19] quantified the suggestion of Wachtman that the fitting parameters B and T_0 are related to the Grüneisen parameter and Debye temperature, respectively. Using the equation of Anderson[19] and assuming

Table 1
Fitting parameters E_0, B and T_0 for describing the Young's modulus as a function of the absolute temperature, and room temperature value of the Young's modulus for $MgSiN_2$, AlN and Si_3N_4[a]

Material/Sample	E_0 (GPa)	B (GPa K^{-1})	T_0 (K)	E_{293} (GPa)
$MgSiN_2$				
RB10 (17.29×8.05×2.15 mm)	277.93 (7)	0.02237 (18)	450 (12)	276.5
	278.24 (16)	0.02190 (38)	403 (25)	276.6
(17.30×5.69×2.15 mm)	286.64 (10)	0.02134 (16)	347 (14)	284.7
	286.76 (9)	0.02136 (15)	332 (11)	284.7
RB31 (17.76×8.06×2.14 mm)	284.78 (6)	0.02281 (14)	424 (9)	283.2
	285.01 (10)	0.02241 (20)	397 (15)	283.3
(17.76×5.85×2.15 mm)	276.45 (7)	0.02251 (17)	422 (11)	274.9
	276.58 (8)	0.02203 (19)	390 (13)	274.9
RB33 (17.54×8.06×2.15 mm)	280.87 (14)	0.02133 (24)	349 (19)	279.0
	280.98 (10)	0.02156 (24)	366 (16)	279.1
(17.55×5.88×2.16 mm)	277.87 (12)	0.02161 (25)	386 (18)	276.2
	277.94 (5)	0.02227 (11)	403 (8)	276.3
Average value $MgSiN_2$	281±4	0.0220±0.0005	389±34	279±4
AlN				
(17.82×8.12×2.12 mm)				
	310.11 (12)	0.02419 (35)	487 (21)	308.8
	310.14 (14)	0.02451 (39)	488 (23)	308.8
(17.80×5.89×2.12 mm)	310.20 (6)	0.02468 (24)	533 (12)	309.0
	310.64 (12)	0.02404 (37)	473 (21)	309.2
(50.23×8.11×2.99 mm)	–	–	–	318.8
	–	–	–	318.8
(50.06×5.88×2.99 mm)	–	–	–	312.9
	–	–	–	312.9
Average value AlN	314±4	0.0244±0.0003	495±26	312±4
Si_3N_4				
H-1 (ø 30×12 mm)[18]	320.41 (13)	0.01508 (24)	445 (28)	319.4

[a] Between parentheses, the 95% confidence interval of the fitting parameters are presented. The experimental error was estimated to equal the standard deviation of the average values.

Table 2
The sound velocities and Debye temperatures at 0 K for $MgSiN_2$, AlN and Si_3N_4

Compound	E_0 (GPa)	ρ_0 (kg m^{-3})	ν (−)	v_l (m s^{-1})	v_t (m s^{-1})	v_s (m s^{-1})	s (−)	θ_0 (K)
$MgSiN_2$	281	3.142×10^{32}	0.246	1.033×10^{4}	5.99×10^{3}	6.65×10^{3}	4	900
AlN	314	3.258×10^{33}	0.245[14]	1.071×10^{4}	6.22×10^{3}	6.90×10^{3}	2	940
Si_3N_4	320	$3.202\times10^{34,a}$	0.267[18]	1.115×10^{4}	6.28×10^{3}	7.00×10^{3}	7	955

[a] Assuming that $\rho_0 = \rho_{293}$ lacking the availability of low temperature data.

Table 3
The Debye temperature θ_0 and θ_{T_0} of $MgSiN_2$, AlN and Si_3N_4 obtained from the fitting parameters E_0 and T_0, respectively as compared to previously reported values obtained from specific heat measurements (θ^C), elastic constants (θ^E) and lattice dynamic calculations (θ^{LD})

Compound	θ_0 (K)	θ_{T_0} (K)	θ^C (K)	θ^E (K)	θ^{LD}
$MgSiN_2$	900	778	829[35]	827[12]	
AlN	940	990	950,[1]1010[36]		800[37]
Si_3N_4	955	890	754,[38] 900[39]	900–1005[40]	

that the Poisson's ratio is temperature independent ($d\nu/dT = 0$) we can calculate B and T_0 using:

$$B = 3(1\text{-}2\nu)\,\frac{3R\gamma\delta}{V_0}$$

and T_0 is very approximately given as:

$$T_0 \approx \theta_0/2.$$

in which ν [−] is the Poisson's ratio, R (8.314 J mol^{-1} K^{-1}) the gas constant, γ [−] the Grüneisen constant,[30] δ (−) the Anderson–Grüneisen constant[31] and V_0 (m^3 mol^{-1}) the specific volume per atom at absolute zero. Using the expressions for γ and δ[19] the equation for B can be written as:

$$B = \frac{s3R}{C_p}\frac{\partial E}{\partial T}$$

in which s (−) is the number of atoms per formula unit and C_p (J mol^{-1} K^{-1}) the heat capacity at constant pressure. It is directly clear that for calculating the value of the fitting parameter B to describe the temperature dependence of the Young's modulus these data themselves are needed. So, this makes an independent evaluation of the fitting parameter B from the present data impossible.

For comparison with other compounds, only few experimental data are available. The experimentally observed value for the fitting parameter B of 0.0220 GPa K^{-1} for $MgSiN_2$, 0.0244 GPa K^{-1} for AlN and 0.0151 GPa K^{-1} for Si_3N_4 are somewhat lower than the values reported for the three oxides investigated by Wachtman (0.048 GPa K^{-1} for Al_2O_3,[17] 0.027 GPa K^{-1} for ThO_2[17] and 0.037 GPa K^{-1} for MgO).[19] The somewhat smaller value for B indicates that the nitrides show a more harmonic bond character as compared to the oxides, as expected from the more covalent nature of nitrides, and considering that the Young's modulus of a fully harmonic bond is temperature independent.

For $MgSiN_2$, AlN and Si_3N_4 the experimentally obtained average T_0 value (see Table 1) was used to estimate the Debye temperature, resulting in 778, 990 and 890 K for $MgSiN_2$, AlN and Si_3N_4, respectively. These θ_{T_0} values are in rough agreement with the θ_0 value (obtained from E_0) and the other reported Debye temperatures for $MgSiN_2$, AlN and Si_3N_4, respectively (see Table 3), indicating the approximate nature of the Anderson equation $\theta \approx 2T_0$.[19]

4. Conclusions

The temperature dependence of the Young's modulus of $MgSiN_2$, AlN and Si_3N_4 can be described very well with $E = E_0 - B \cdot T\exp(-T_0/T)$. The Debye temperatures estimated from E_0 and T_0 are in rough agreement with each other, and with previously reported values obtained in different ways. The values of the fitting parameter B determined for our nitrides are lower than those previously reported for oxides. This is ascribed to the more harmonic nature of bonds in nitrides as compared to oxides resulting in a relatively temperature independent Young's modulus.

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