Modeling the Thermal Conductivity of Mullite/Cordierite Composites

S.C. Beecher and D.G. Onn

Applied Thermal Laboratory, Department of Physics and Astronomy
University of Delaware, Newark, Delaware 19716 (USA)

ABSTRACT

The thermal conductivity (κ) has been measured for a series of mullite/cordierite composites in the temperature range 20 to 300 K. The Klemens-Callaway model, which is used to describe the temperature dependence of κ for crystalline materials, has been applied to the experimental results. This model incorporates three phonon-scattering terms, that include the effect of impurities, grain boundaries and phonons. The compositional dependence shows the characteristic form indicating the possibility of the formation of solid solutions.

INTRODUCTION

Mullite/cordierite composites represent an important technological class of materials for the electronics packaging industry. Both mullite and cordierite have a lower dielectric constant and thermal expansion coefficient than either alumina, Al_2O_3, or aluminum nitride, AlN, which are the most widely used substrate materials, but mullite and cordierite also have a much lower thermal conductivity. Literature values for these quantities are shown in Table 1 along with the properties of silicon, Si (Chowdry and Sleight 1987).

The composite materials studied in this investigation were prepared by Richard Anderson (1987) at Rutgers University. The primary goals of his research were to produce composite materials with a thermal expansion coefficient nearly equal to that of silicon and to measure their mechanical and dielectric properties. The secondary goal of his research was to determine suitable models for the properties of these composite materials. We will give a brief description of the material synthesis and the results of some of Anderson's measurements in the next section and, where germane to the topic, in subsequent sections. It was the purpose of this investigation

TABLE 1

Dielectric and thermal properties of selected materials.

Material	Dielectric constant	Thermal Expansion Coefficient (10^{-6} C^{-1})	Thermal Conductivity ($W.m^{-1}.K^{-1}$)
Alumina	9.6	7.2 - 8.6	25 - 35
AlN	8.8	4.5	60 - 320
Cordierite	5 - 6	1 - 2	1 - 2
Mullite	6.6	5.5	4.0
Si	12	3.5	130

to measure and model the temperature dependence of the thermal conductivity of these composites. The notation used to describe these composites is weight% Mullite / weight% Cordierite.

MATERIAL FABRICATION AND CHARACTERIZATION

Mullite is a naturally occuring orthorhombic mineral with the stoichiometric formula $3Al_2O_3:2SiO_2$. It is possible to form mullite with a range of ratios of alumina to silica. These ratios are from 3:2 to 2:1. More important to this research is that mullite forms solid solutions, which is indicated by the varying ratio of alumina to silica. The extent of stable solid solution is given to be 60 to 63 mole percent alumina. Mussler and Shafer (1984) have suggested that solid solutions might occur when mullite and cordierite are formed into composites. The stated purity of the as-received mullite powder was > 99%, although no chemical analysis was given. Initial X-ray analysis indicated the presence of small amounts of alumina in the as-received powder.

Cordierite has the stoichiometric formula $2MgO:2Al_2O_3:5SiO_2$, but several polymorphic forms of cordierite exist. The high cordierite form is a psuedo-hexagonal structure. Prolonged heating of the high cordierite form at high temperatures results in the transformation to the low cordierite form, which is stable and possesses an orthorhombic structure. High cordierite was used in the composite fabrication. The stated purity of the as-received cordierite powder was >99%, although no quantitative analysis was performed to determine whether any impurities were present.

Initially the powder of each material was weighed and mixed in the desired ratio. 100 g of each composite were then mixed for one hour in a plastic container that was rotated on a ball mill rack. The powders were then milled and comminuted in an attritor mill for 24 hours using mullite as the milling media mixed with 150 ml of distilled water. After the milling was complete the suspension was poured through a 325 mesh sieve and dried in an electric dryer at 100 $^\circ$C. Prior to cold pressing the composites, the powder was broken up, mixed with about 5 weight% of a 1.5 weight% aqueous solution of superloid binder and then passed through a 20 mesh sieve to form granules. The granules were placed in a die and cold pressed at 5000 psi. After pressing, the samples were placed on mullite setters and fired in an electric kiln. Initially the samples were heated to 500 $^\circ$C and held for 4 hours. They were then heated to the final sintering temperature at 225 $^\circ$C/hr and held there for one hour. The final sintering temperatures are shown in Table 2. After the required time the furnace was cooled to room temperature at 5 - 10 $^\circ$C/min. The final step was cutting the samples for measurements.

TABLE 2

Sintering temperatures and quantitative X-ray analysis results for phase composition of the Mullite/Cordierite composites.

Sample	Sintering Temperature $^\circ$C	weight% Mullite	weight% Cordierite
10/90	1420	10.6	89.4
25/75	1430	30.4	69.6
50/50	1440	48.2	51.8
75/25	1440	79.9	20.1
90/10	1445	100	-

X-ray Diffraction Studies

The results of the X-ray diffraction analysis indicated that there was a small amount of alumina in the 90/10 and 75/25 samples, and that there was no cordierite present in the 90/10 sample. Zircon was mixed with the prepared samples for the X-ray analysis as a reference material so that the amount of cordierite and mullite in the final processed material could be determined. Table 2 shows the results of this analysis. The increase in the amount of mullite in the 25/75 and 75/25 samples was attributed to excess mullite added in the milling stage. The alumina detected in

samples 75/25 and 90/10 was attributed to the alumina detected in the as-received powders. Cordierite was detected in the 90/10 sample prior to sintering but was undetected after sintering. A possible explanation was the melting of the cordierite to form mullite and glass.

Density Measurements

The density, ρ, was measured for each sample mechanically (a) by measuring the volume and the mass, and (b) by Archimedes' principle. The results of the measurements are shown in Table 3 as ρ_{mech} and ρ_{Arch} respectively. Literature values for the densities of mullite and high cordierite, given as 3.26 g/cm^3 and 2.50 g/cm^3 respectively, were used to determine the theoretical density for each composite, which is shown in Table 3. Also shown in Table 3 are the volume fractions of each phase including porosity. The matrix volume fraction v_m is considered to be the cordierite component, the filler volume fraction v_f is the mullite, and v_p is the pore volume fraction. From this table, samples 10/90 and 25/75 appear to be fully dense while the remaining samples have a small amount of porosity present, which must be taken into account for the thermal conductivity analysis.

TABLE 3

Mass and density measurements of the Mullite/Cordierite composites.

Sample	mass (g)	ρ_{th} (g.cm^{-3})	ρ_{mech} (g.cm^{-3})	ρ_{Arch} (g.cm^{-3})	v_p	v_f	v_m
10/90	0.587	2.56	2.57	2.58	0	0.078	0.922
25/75	0.460	2.65	2.65	2.67	0	0.203	0.797
50/50	0.445	2.83	2.81	2.85	0.007	0.431	0.562
75/25	0.565	3.07	2.92	2.98	0.036	0.672	0.292
90/10	0.671	3.18	3.07	3.13	0.030	0.847	0.123

EXPERIMENTAL TECHNIQUE

In recent years researchers have developed various new methods for measuring the thermal conductivity of materials. These methods usually involve the measurement of the thermal diffusivity, α, by temperature transient techniques. κ is related to α by

$$\kappa = \alpha.\rho.C_p, \tag{1}$$

where C_p is the specific heat of the material and ρ is its density. The basic principle

behind transient methods is to deposit a short burst of energy onto one surface of the material, whose geometry is in the form of a thin slab, either cylindrical or rectangular in shape. After the energy has been deposited, the time-temperature history of the opposite face is monitored. The diffusivity, α, can then be related to the time, $t_{1/2}$, it takes for the temperature of this face to reach half its maximum value by

$$\alpha = \frac{0.1388 \; l^2}{t_{\frac{1}{2}}}, \tag{2}$$

where l is the sample thickness. If the amount of energy deposited is unknown then C_p must be determined by another method in order to calculate κ.

This method for the determination of α was first proposed by Parker et. al. (1961), who employed radiant energy for the heating source, and hence another method was used to determine C_p. Giedd and Onn (1989) modified this method by using a square pulse of electrical energy which is deposited through a colloidal graphite resistance heater sprayed onto the surface of the sample. By measuring the voltage, current and duration of the pulse, the amount of energy deposited, Q, can be determined. From the overall temperature rise ΔT and the mass, m, of the sample, C_p can be determined by

$$C_p = \frac{Q}{m \Delta T}. \tag{3}$$

Using this method we can simultaneously determine C_p and α, and hence by Equation 1, κ. The experimental apparatus is mounted on the cold finger of a closed-cycle helium refrigeration system which allows us to make measurements from room temperature down to 20 K.

THEORY

The temperature dependence for the thermal conductivity for dielectric crystalline materials can be described by

$$\kappa = \frac{k_B}{2\pi^2 v} \left(\frac{k_B 2\pi T}{h} \right)^3 \int_0^{\frac{\theta_D}{T}} \tau(x) \; \frac{x^4 e^x dx}{(e^x - 1)^2}, \tag{4}$$

where k_B is Boltzmann's constant, v is the sound velocity, h is Planck's constant, θ_D is the Debye temperature, and T is the temperature (Berman 1976). Theoretical

predictions of κ depend on the assumptions made about the phonon relaxation time τ or its inverse, the scattering rate. In the derivation of this expression it was assumed that the material is an isotropic elastic continuum.

The overall phonon scattering rate τ^{-1} can be considered to be the sum of three terms, boundary scattering $\tau^{-1}{}_b$, impurity scattering $\tau^{-1}{}_i$, and phonon-phonon (Umklapp) scattering $\tau^{-1}{}_u$. The expression for τ^{-1} is then

$$\tau^{-1} = \tau_b^{-1} + \tau_i^{-1} + \tau_u^{-1}. \tag{5}$$

The scattering rate for Normal processes can be ignored in this analysis since in the majority of physical cases resistive processes will dominate (Kittel 1986, Berman and Brock 1965).

The boundary scattering rate can be written as

$$\tau_b^{-1} = \frac{1.12\ v}{d}, \tag{6}$$

where d is the crystal dimension for a pure single crystal or the grain size for polycrystalline material (Casimir 1938).

Klemens (1951) proposed that the impurity scattering of phonons was similar to that for Raleigh scattering of light. This leads to a scattering rate given by

$$\tau_i^{-1} = I\omega^4, \tag{7}$$

where ω is the phonon frequency, which is proportional to the temperature; I is a temperature-independent quantity. For point defects the expression given by Klemens (1958) is

$$I = \frac{ca^3}{4\pi v^3}\left(\frac{\Delta M}{M}\right)^2, \tag{8}$$

where c is the relative defect concentration, a^3, the atomic volume, M, the normal mass and ΔM is the mass difference.

The Umklapp scattering term has been treated by various authors. From the theory of Umklapp processes Klemens (1956) gives an expression for the Umklapp scattering rate as

$$\tau_u^{-1} = A\omega^2 T e^{\left(\frac{-B}{T}\right)},$$ (9)

where A is a proportionality constant and B is a constant proportional to Θ_D.

Callaway (1960) assumed that the temperature dependence in the pre-exponential varied as T^3 instead of T. His writes his expression for Umklapp processes as

$$\tau_u^{-1} = B(T)T^3\omega^2,$$ (10)

where B(T) contains the exponential. Berman (1965) suggests that the pre-exponential varies as T^2. Parrott and Stuckes (1975) point out that there is no equation that can be given for the Umklapp scattering rate which can interpolate between the low temperature behavior of the thermal conductivity, where the Umklapp term is insignificant, and the high temperature behavior, where $\tau^{-1}_u \sim \omega^2 T$. The frequency dependence given in these expressions was derived on the basis of an isotropic model. Anisotropy may produce additional collisions with different frequency dependencies.

RESULTS AND DISCUSSION

The results of the measurements of κ for the composites are shown in Figure 1. Two samples, 10/90 and 90/10, show a peak in κ between about 125 and 150 K. The remaining three samples appear to show a much smaller peak in the same temperature range. For these three samples it appears that κ is almost constant, within experimental error, until it starts to decrease at about 125 K.

Prior to analyzing the temperature dependence of κ for these materials the experimental data was corrected for porosity using Kerner's (1956) composite thermal conductivity model. His expression for the thermal conductivity for a two phase composite is

$$\kappa_{eff} = \kappa_m \left(\frac{2\kappa_m + \kappa_f + 2v_f(\kappa_f - \kappa_m)}{2\kappa_m + \kappa_f - v_f(\kappa_f - \kappa_m)}\right),$$ (11)

where in terms of the thermal conductivites and volume fractions for the mullite-cordierite composites, κ_{eff} is the measured κ, and v_f and κ_f are the volume fraction and thermal conductivity of the pores, respectively. In this case $\kappa_f = 0$. κ_m is the thermal conductivity of the fully dense composite.
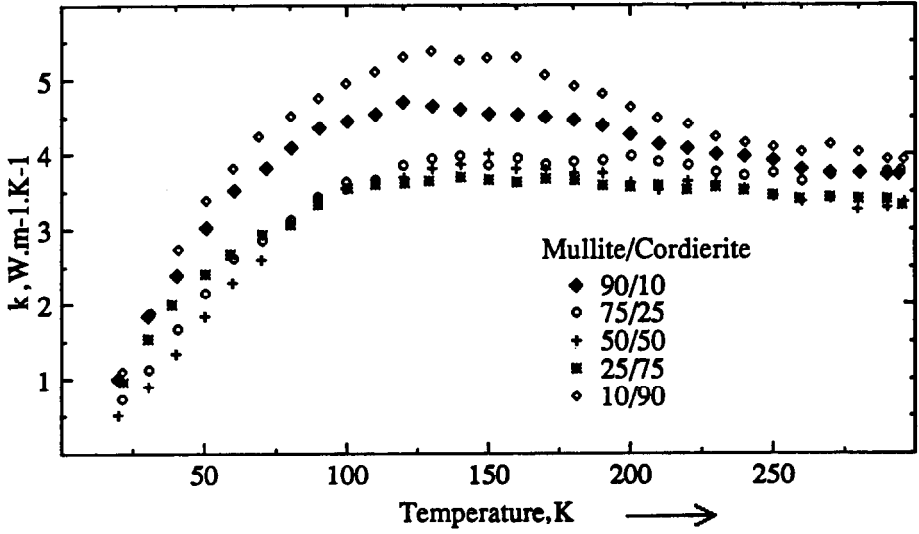
Fig. 1. Experimental κ for the Mullite/Cordierite composites. The error bars were omitted for clarity and are 10% of the value shown.

By setting $\omega = 2\pi k_B T/h$ and substituting the forms for the scattering rates into Equation 4, it can be rewritten as

$$\kappa = \frac{k_B}{2\pi^2}\left(\frac{2\pi k_B T}{h}\right)\int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x dx}{\left(v/d + I't^4 + A'T^3 x^2 e^{\frac{B}{T}}\right)(e^x - 1)^2}, \tag{12}$$

where

$$I' = I\left(\frac{2\pi k_B}{h}\right)^4 \tag{13}$$

is called the impurity parameter and

$$A' = A\left(\frac{2\pi k_B}{h}\right)^2, \tag{14}$$

the Umklapp A' parameter. Once the Debye temperature and sound velocity are known a nonlinear least-squares fit can be performed to the data using Equation 12

with four free parameters. Since the nature of the impurities is not known, whether substitutional or vacancy, and due to the complicated structure of the components of the composites, the impurity parameter will be give by Equation 13. Similarly the Umklapp parameters will be given as B and A'.

The Debye temperature for each composite was determined by fitting the specific heat data to the Debye function (Beecher 1990). The results of this fit are shown in Table 4, together with the results of Anderson's measurement of the sound velocity. Also shown in Table 4 are the parameters for each sample as determined from a nonlinear least-squares fit to the porosity-corrected experimental data. The errors in the values were estimated by adding and subtracting 10% of each data point and refitting. The numbers shown are the average of the three fits and their standard deviations. The theoretical predictions are shown in Figures 2 through 4.

TABLE 4

Debye temperatrue, sound velocity and parameters from fit to κ for the Mullite/Cordierite composites using the Klemens-Callaway model.

Sample	Θ_D (K)	V $(10^5$ $cm^2.sec^{-1})$	A' $(10^4$ $K^{-3}.S^{-1})$	B (K)	I' $(K^{-4}.S^{-1})$	d (μm)
10/90	700	5.05	13 ± 1	291 ± 1	400 ± 40	0.11 ± 0.01
25/75	880	5.19	5.5 ± 0.5	250 ± 2	830 ± 80	0.14 ± 0.01
50/50	857	5.56	13 ± 1	194 ± 1	240 ± 20	0.032 ± 0.003
75/25	875	5.70	5.9 ± 0.6	118 ± 1	340 ± 30	0.057 ± 0.006
90/10	1105	5.72	10.2 ± 0.1	270 ± 1	440 ± 40	0.14 ± 0.01

The trends in the parameters do not vary as smoothly as one would expect when the amount of mullite is increased. Both phases are crystalline but the parameters and the trends in the shape of the thermal conductivity curves suggests that the structure of the material changes. A' is roughly constant, or at most changes by a factor of two, while the B parameter decreases with increasing the amount of mullite, until sample 90/10, where it reaches the second highest value. The magnitude of the impurity parameter reflects the complicated structure of both sets of materials. The interesting parameter is the grain size for these composites. The grain sizes for samples 50/50 and 75/25 are 2 to 3 times smaller than for the other samples. Recently results have been published on the properites of mullite/cordierite composites prepared by the sol-gel process by Ismail et. al. (1990). They prepared composites with 80, 70, 60, 50, and 40 weight% mullite, and their results for the crystallite size are consistent with our fit parameters. They give the crystallite sizes for the 80 and 50 weight% mullite samples as 0.055 μm and 0.0375 μm,

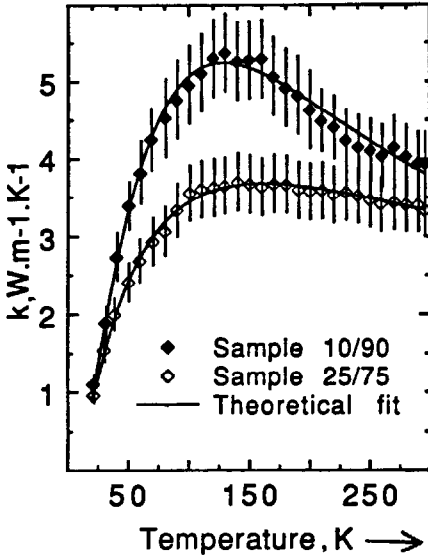Fig. 2. Theoretical prediction of κ using the Klemens-Callaway model for samples 10/90 and 25/75.
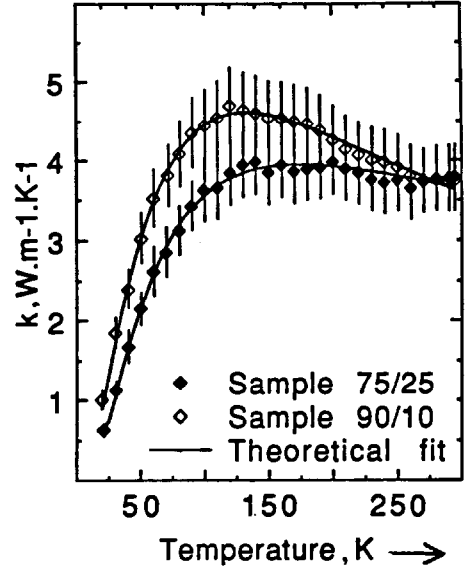
Fig. 3. Theoretical prediction of κ using the Klemens-Callaway model for samples 90/10 and 75/25.

respectively. These values are almost identical with those of our 75 and 50 weight% mullite samples. They observed the growth in the mullite with the addition 20 weight% cordierite compared to the pure mullite sample. Further additions of cordierite reduced the crystallite size of the mullite. They also conclude from Transmission Electron Microscopy and Energy Dispersive X-ray Diffraction measurements that in the high weight% mullite composites (>70 weight% mullite), the cordierite melted to form a glassy phase.

The thermal conductivity for these composites as a function of mullite at three different temperatures is shown in Figure 5. The first thing to notice from this figure is the concave behavior of κ as the amount of mullite is increased. This behavior may be attributable to microcracking or to the formation of solid solutions. Kingery (1959) has observed similar results for an alumina-mullite composite system and attributes the results to flat grain-boundary cracks due to internal stress. This appears reasonable considering the large difference in thermal expansion coefficients shown in Table 1. However the thermal expansion coefficients of mullite and cordierite are very similar. Anderson measured the thermal expansion coefficients for these composites and found no hysteresis in the results indicating that there were no microcracks. The behavior of κ can most probably be attributed to the formation of solid solutions.
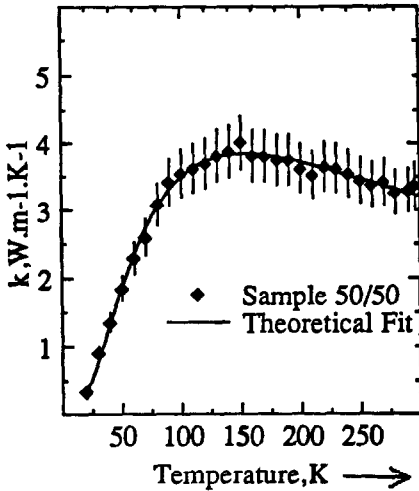
Fig. 4. Theoretical prediction of κ using the Klemens-Callaway model for sample 50/50.
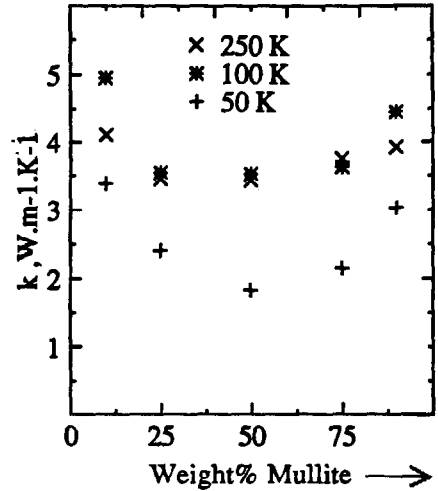

Fig. 5. κ as a function of weight% mullite.

CONCLUSIONS

We have measured the temperature dependence of κ for a series of mullite/cordierite composites. The variation in $\kappa(T)$ when increasing the amount of mullite indicates that changes have occured in the materials when the composites were formed. The 10 and 90 weight% mullite samples show a maximum in $\kappa(T)$, while the intermediate compositions show a behavior that appears to be that of an amorphous or a complicated microcrystalline material. The Klemens-Callaway model for dielectric crystalline materials, using three phonon scattering terms, was used to model $\kappa(T)$. The parameters determined from the fit to the porosity-corrected experimental data do not follow a smooth trend when the amount of mullite is increased. The grain sizes for two samples, the 50 and 75 weight% mullite samples, are almost identical with the grain sizes for the 50 and 80 weight% mullite samples of Ismail et. al.(1990). It is remarkable that our grain sizes were determined by fitting the experimental data to the Klemens-Callaway model, while theirs was determined from X-ray analysis. This shows that the Klemens-Callaway model seems to be capable of providing at least a semi-quantitative description for these materials.

Further confirmation that modifications have occured in these materials is that the composite κ shows a dip when the amount of mullite is increased and the dip is more pronounced as the temperature is decreased. This trend in κ suggests that the

formation of a solid solution has occured. This result has also been confirmed by Ismail et. al. in the study of mullite/cordierite composite produced by a sol-gel process.

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