

# ELASTIC PROPERTIES OF MULLITE AND MULLITE-CONTAINING CERAMICS

## PART 1: THEORETICAL ASPECTS AND REVIEW OF MONOCRYSTAL DATA

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*In this first part of a two-paper set on the elastic properties of mullite and mullite ceramics the current literature is reviewed and, based on the available monocrystal data, a mutually consistent average set of elastic constants for polycrystalline mullite materials at room temperature is calculated and optimized via minimization of the total average relative root mean square (RMS) deviation. Based on the results of this paper, the recommended values of adiabatic elastic constants are 224.9 GPa for the Young's modulus, 87.8 GPa for the shear modulus, 170.9 GPa for the bulk modulus and 0.281 for the Poisson ratio. The RMS deviation of this set is lower than for any other set, and thus these values exhibit a high degree of mutual consistency with respect to the elasticity standard relations. Micromechanical upper bounds and model relations are summarized for describing the porosity dependence of elastic moduli, and a simple relation is used to estimate the difference between adiabatic and isothermal elastic constants. The results show that this difference increases slightly with temperature, but is not larger than 4 % even at 1500°C. In particular, for the Young's modulus the difference remains below 0.5 %. That means, the difference between adiabatic and isothermal Young's moduli will usually be unmeasurably small and negligible in practice.*

### INTRODUCTION

Mullite is the most important crystalline phase in many silicate ceramics (e.g. porcelain, stoneware, earthenware), refractories (e.g. fireclay/chamotte, sillimanite bricks) and ceramic composites [1, 2]. Therefore its elastic properties are of utmost practical importance throughout ceramic science and engineering. In particular, for all predictive calculations concerning the effective elastic constants (or moduli) of multiphase composites the elastic constants (moduli) of mullite as a single phase must be reliably known. Such knowledge is generally not available from the textbook literature, because porosity effects and compositional variations are usually not taken into account with due care (grain size effects can be assumed to be negligible, unless nanocrystalline materials are considered [3]). In fact, reliable values for the elastic constants of dense (i.e. pore-free) isotropic polycrystalline materials can only be obtained by calculating the Voigt-Reuss-Hill averages of the elastic moduli from the components of the elasticity tensor for mullite single crystals, more precisely from

the elements of the stiffness matrix and its inverse, the compliance matrix. Today these values are available in the literature. In particular, the groups of Kriven and Schneider have performed extensive and very detailed experimental studies of the single-crystal elastic properties of mullite, not only for room temperature, but up to temperatures of 1400°C, using resonant ultrasound techniques and Brillouin spectroscopy [4-8]. However, although the data previously scattered in the literature have been collected in the monograph by Schneider and Komarneni [2] and in a more recent review article [9], it seems that a final comparison of the corresponding Voigt-Reuss-Hill averages of the effective Young's moduli for all data sets has not been performed and published so far. For example, on p. 143 of the mentioned monograph, Schneider presents a comparative table of single-crystal stiffness and compliance data, but only the Reuss values of the bulk moduli are calculated from these directly, and the Young moduli, shear moduli and bulk moduli listed elsewhere in the same book (p. 313) by Okada and Schneider are evidently based only on one of these data sets [7].

In this contribution we summarize the current knowledge on the elastic properties of mullite and mullite ceramics in a way that leads to an updated final set of room temperature values for the elastic constants that is mutually consistent with respect to the “elasticity standard relations“ (i.e. the mutual interrelations between the elastic constants of isotropic materials [10]) and can thus be recommended as a reliable input information for all subsequent calculations of multiphase ceramics and composites, e.g via the Hashin-Shtrikman bounds [11]. Although the optimized data set recommended by Hildmann et al. [7] is very consistent indeed, leading to total average relative root square deviations (defined below) of only  $1.2 \times 10^{-4}$  for the elastic constants (for comparison: the other three data sets and Ledbetter’s data set before optimization exhibit relative root square deviations between  $4.7$  and  $8.5 \times 10^{-3}$ ), the present paper shows that when all available single-crystal data are taken into account, an average data set can be found that is even more consistent and precise than Hildmann’s set, resulting in root mean square deviations as low as  $1.7 \times 10^{-5}$  for the elasticity constants at room temperature.

With respect to the importance of mullite in refractories, the temperature dependence of the elastic constants is briefly mentioned as well. Since it is common practice in the field of refractories to test mechanical properties by static or very slow (quasistatic) tests, it is important to dispose of a realistic estimate of the difference between isothermal and adiabatic elastic constants. Such an estimate can be given (for any temperature) when – in addition to the bulk modulus – the specific heat and the (true) coefficient of thermal expansion is known for the temperature in question. Therefore also this point is addressed in the present paper. In the second part of this two-paper set, experimental results will be presented concerning the Young’s moduli of mullite and mullite-containing ceramics, measured via the impulse excitation technique, including their temperature dependence, and compared to the theoretical predictions.

### Effective elastic constants of polycrystalline materials from monocrystal data

The behavior of linearly elastic anisotropic materials is described by Hooke’s law in the form

$$T_{ij} = C_{ijkl} E_{kl} \quad (1)$$

where  $T_{ij}$  is the Cauchy stress tensor,  $C_{ijkl}$  the stiffness tensor (elasticity tensor) and  $E_{kl}$  the small strain tensor [10]. Alternatively, the constitutive equation of linearly elastic materials can be written in the form

$$E_{ij} = S_{ijkl} T_{kl} \quad (2)$$

(inverse Hooke’s law), where  $S_{ijkl}$  is the compliance tensor, i.e. the inverse of the stiffness tensor.

Due to the symmetry of the stress and strain tensors, the number of components of the stiffness and

compliance tensors is reduced from a total of 81 to 36 independent ones [10]. Thus, it is possible to represent these fourth-order tensors alternatively in the form of  $(6 \times 6)$  matrices, and to express Hooke’s law and inverse Hooke’s law in matrix notation (engineering notation) as

$$\sigma_i = C_{ij} \varepsilon_j \quad (3)$$

$$\varepsilon_i = S_{ij} \sigma_j \quad (4)$$

respectively, where the abstract 6-dimensional vectors  $\sigma_i$  and  $\varepsilon_i$  now represent the 6 independent components of the stress and strain tensors and the indices are renamed according to the engineering convention, see e.g. [10].

In the most general case of anisotropy (triclinic monocrystals) the  $(6 \times 6)$  stiffness or compliance matrices or, alternatively, the fourth-order stiffness or compliance tensors, have 36 elastic constants or coefficients, respectively, but only 21 of these are independent, since the stiffness and compliance matrices are additionally symmetric with respect to their diagonals (so-called Green elasticity or hyperelasticity), cf. [10]. For materials of higher symmetry (monocrystals, polycrystalline or multiphase materials) the number of independent elastic constants is further reduced, so that for orthorhombic monocrystals there are only 9 independent elastic constants. The stiffness matrix in the latter case is

$$(C_{orthorhombic}) = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{21} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{31} & C_{32} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix}. \quad (5)$$

In the case of isotropic materials (i.e. the case of highest symmetry) the stiffness matrix is greatly simplified, because the following relations hold between the matrix elements:

$$\begin{aligned} C_{11} = C_{22} = C_{33}, \quad C_{12} = C_{23} = C_{31}, \\ C_{44} = C_{55} = C_{66} = \frac{1}{2}(C_{11} - C_{12}) \end{aligned} \quad (6)$$

That means, for isotropic materials only 2 of these elastic constants are independent and, using the definitions  $C_{12} \equiv \lambda$  and  $C_{44} \equiv \mu$ , the stiffness matrix of isotropic materials can be written as [10]

$$(C_{isotropic}) = \begin{pmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{pmatrix}. \quad (7)$$

Note that all stiffness matrix elements (elastic constants), including  $\lambda$  and  $\mu$  (the so-called Lamé constants) have units [GPa] and are therefore elastic moduli (in contrast to the dimensionless Poisson ratio, which is an elastic constant, but not an elastic modulus [10]).

Of course, the two Lamé constants occurring in the stiffness matrix (7) are only one possible choice of elastic constants for isotropic materials. Depending on the problem or application in question, other elastic constants may be more convenient, e.g. the tensile modulus (Young's modulus)  $E$  (units [GPa]), the shear modulus  $G$  ([GPa]), the bulk modulus  $K$  ([GPa]) and the Poisson ratio  $\nu$  (dimensionless). Only two (independent) elastic constants are sufficient to calculate all other constants and thus to describe the elastic behavior of isotropic materials completely. For easy reference we list the interrelations between the elastic constants (denoted as "elasticity standard relations" in the sequel) needed in this paper:

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) = \frac{9KG}{3K + G}, \quad (8)$$

$$G = \frac{E}{2(1 + \nu)} = \frac{3K(1 - 2\nu)}{2(1 + \nu)} = \frac{3EK}{9K - E}, \quad (9)$$

$$K = \frac{E}{3(1 - 2\nu)} = \frac{2G(1 + \nu)}{3(1 - 2\nu)} = \frac{EG}{3(3G - E)}, \quad (10)$$

$$\nu = \frac{3K - 2G}{2(3K + G)} = \frac{E - 2G}{2G} = \frac{3K - E}{6K}. \quad (11)$$

Polycrystalline materials consisting of randomly oriented crystallites are usually isotropic, although the individual crystallites contained in the microstructure are anisotropic. Sometimes such microstructures are called "quasi-isotropic" or "statistically isotropic", but this should not obscure the fact that from a macroscopic (non-local, continuum) engineering point of view these materials are just isotropic and thus can be described by only two elastic constants. Therefore it is clear that the effective elastic constants of polycrystalline materials are related to the elastic constants of the crystallites by orientational averaging. For this calculation not only the stiffness matrix is needed, but also the compliance matrix, which is obtained from the former by matrix inversion [12].

According to Voigt's "isostrain assumption" [13], the effective tensile modulus of a macroscopically isotropic polycrystalline material is

$$E_V = \frac{(A - B + 3C)(A + 2B)}{2A + 3B + C}, \quad (12)$$

the effective shear modulus

$$G_V = \frac{A - B + 3C}{5}, \quad (13)$$

and the effective bulk modulus

$$K_V = \frac{A + 3B}{3}. \quad (14)$$

In these expressions  $A, B, C$  are given by

$$A = \frac{C_{11} + C_{22} + C_{33}}{3}, \quad (15)$$

$$B = \frac{C_{12} + C_{23} + C_{31}}{3}, \quad (16)$$

$$C = \frac{C_{44} + C_{55} + C_{66}}{3}. \quad (17)$$

Similarly, according to Reuss's isostress assumption [14], the effective tensile modulus of a macroscopically isotropic polycrystalline material is

$$E_R = \frac{5}{3X + 2Y + Z}, \quad (18)$$

the effective shear modulus

$$G_R = \frac{5}{4X - 4Y + 3Z}, \quad (19)$$

and the effective bulk modulus

$$K_R = \frac{1}{3(X + 2Y)}. \quad (20)$$

In these expressions  $X, Y, Z$  are given by

$$X = \frac{S_{11} + S_{22} + S_{33}}{3}, \quad (21)$$

$$Y = \frac{S_{12} + S_{23} + S_{31}}{3}, \quad (22)$$

$$Z = \frac{S_{44} + S_{55} + S_{66}}{3}. \quad (23)$$

Using the aforementioned elastic standard relations, the corresponding Voigt and Reuss values of the Poisson ratios can be calculated as well. Hill [15] has shown that the Voigt and Reuss values represent upper and lower bounds, respectively, of the effective elastic moduli  $M$  of macroscopically isotropic polycrystalline materials ("Hill's theorem"), i.e.

$$M_R \leq M \leq M_V, \quad (24)$$

and further experience with the effective elastic properties of polycrystalline materials has shown that the Voigt bound and the Reuss bound are sufficiently close to neglect the difference between different means [16]. Therefore, following Hill's recommendation [15], it is common practice to use the arithmetic mean of the Voigt and Reuss values,

$$M_{VRH} = \frac{M_V + M_R}{2} \quad (25)$$

(where  $M$  denotes any of the above moduli), as a valid estimate of the effective elastic modulus of dense isotropic polycrystalline materials ("VRH average"). Of course, this averaging procedure can be used for adiabatic

or isothermal elastic constants at any temperature, as long as the material can be considered as purely (and linearly) elastic.

Of course, scatter of experimental data, rounding errors and the fact that taking the arithmetic (and not e.g. the geometric) average is to a certain degree an arbitrary choice, may cause certain errors in the calculated VRH averages so that these need not be entirely consistent with respect to the aforementioned elastic standard relations, resulting in a certain degree of mutual inconsistency of the values. However, it is usually possible to find an optimized set of elastic constants with highest degree of mutual consistency by changing one or two of the calculated VRH averages by a very small amount (typically not more than 100 MPa), and thus uncertainties of this kind can be largely eliminated. As a simple measure of mutual consistency one may choose relative root mean square (RMS) deviations defined as follows:

$$\zeta_1 = \sqrt{\left(\frac{M_1(M_{VRH2}, M_{VRH3}) - M_{VRH1}}{M_{VRH1}}\right)^2}, \quad (26)$$

where  $M_1(M_{VRH2}, M_{VRH3})$  is the value of a selected modulus (here denoted by index 1) as calculated from the VRH averages of two other moduli (indices 2 and 3) and  $M_{VRH1}$  is the VRH average of this modulus calculated directly from its Voigt and Reuss values (upper and lower bounds). Thus, for each individual elastic modulus ( $E, G, K$ ) the average (arithmetic mean) relative RMS deviation is given as

$$\Delta_i = \frac{\zeta_1 + \zeta_2 + \zeta_3}{3} . \quad (27)$$

where the subscript  $i$  denotes the type of modulus considered and  $\zeta_2$  and  $\zeta_3$  are obtained by cyclic permutation of the indices in Equation (26). In fact, this measure can be used not only for the elastic moduli, but also for the Poisson ratio, i.e. for all elastic constants. Arithmetic averaging then yields the total average relative RMS deviation:

$$\Delta = \frac{1}{N} \sum_{i=1}^N \Delta_i , \quad (28)$$

where  $N$  is the number of all types of elastic constants considered. Minimization of this measure yields the desired optimized set of elastic constants. It should be recalled that this optimization procedure is based on the fact that the calculated VRH averages should be mutually consistent with respect to the elasticity standard relations for isotropic materials, and only two elastic constants should enable a calculation of the others with highest possible precision.

#### Temperature dependence and difference between isothermal and adiabatic elastic constants

Similar to most other material properties, elastic constants (and of course also its tensorial counterparts,

the stiffness tensors) are temperature-dependent, e.g. for the Young's modulus

$$E = E(T), \quad (29)$$

with  $T$  being the absolute (thermodynamic) temperature in Kelvins [K]. From the theoretical point of view, such a temperature dependence arises naturally within the framework of linear thermoelasticity when temperature is chosen as the independent variable [17]. Elastic constants measured at constant temperature via static (or quasi-static, i.e. sufficiently slow) techniques, typically bending tests, are called isothermal. However, an alternative – completely equivalent and equally valid – theory of linear thermoelasticity can be constructed by replacing the temperature as the independent variable by the specific entropy  $s$  [17, 18]. In this case we have to consider entropy-dependent (instead of temperature-dependent) elastic constants, e.g. for the Young's modulus

$$\tilde{E} = \tilde{E}(s) . \quad (30)$$

Elastic constants measured at constant entropy, typically via dynamic methods (e.g. sound wave or resonant frequency techniques), are called isentropic or adiabatic. In this case the process mechanism exploited for measuring (wave propagation or vibration) is too fast for the material to attain thermal equilibrium, i.e. the entropy (heat content) is constant during the measurement, but not necessarily the temperature. That means, strictly speaking, the temperature is allowed to vary during the measurement or, put differently, the temperature is influenced by the measurement itself (not due to dissipative loss mechanisms, of course, which are excluded for purely elastic behavior, but because the atomic motion itself represents de facto an increase in temperature). However, the change in temperature due to atomic motion is usually unmeasurably small and need not to be taken into account when the temperature dependence of elastic constants (isothermal or adiabatic) is considered.

Values of isothermal elastic constants are usually different from the adiabatic ones. In particular, the isothermal and adiabatic bulk moduli are related by the ratio of specific heats at constant pressure (stress) and at constant volume (deformation),  $c_p$  and  $c_v$ , respectively, i.e.

$$\frac{\tilde{K}}{K} = \frac{c_p}{c_v} , \quad (31)$$

and since  $c_p$  is always higher than  $c_v$ , the adiabatic bulk modulus is always higher than the isothermal one [19,20]. Note, however, that on theoretical grounds the isothermal and adiabatic shear moduli are always equal [17-19], i.e.

$$\tilde{G} = G . \quad (32)$$

Since, according to the aforementioned elasticity standard relations, all elastic constants of isotropic materials can be calculated when two of them are known, the knowledge of the  $c_p/c_v$  ratio according to Equation

(31) alone is sufficient for calculating the differences between isothermal and adiabatic values for all elastic constants. This ratio can be calculated when the density, specific heat, (linear) thermal expansion coefficient and bulk modulus are known for the temperature in question. Note, however, that the bulk modulus in the well-known thermodynamic relation [21, 22]

$$c_p - c_V = TVK(3\alpha)^2, \quad (33)$$

is the isothermal bulk modulus and, in order to obtain the  $c_p/c_V$  ratio, the  $c_V$  value has to be estimated via the Grüneisen parameter [18]. Therefore, when only the adiabatic bulk modulus is available (as is often the case), this relation has to be modified using Equation (31) and the  $c_p/c_V$  ratio is then given as

$$\frac{c_p}{c_V} = 1 + \frac{TK(3\alpha)^2}{\rho c_p} = 1 + \frac{T\tilde{K}(3\alpha)^2}{\rho c_p}. \quad (34)$$

where  $K$  and  $\tilde{K}$  are the isothermal and adiabatic bulk moduli, respectively. Of course, the results of these calculations are critically dependent on the thermal expansion coefficients, because Equations (33) and (34) depend on  $\alpha$  squared.

It follows from thermodynamics that the elastic constants (both isothermal and adiabatic) will become temperature-independent at sufficiently low temperatures (i.e. when approaching absolute zero, also the temperature coefficient of the elastic constants goes to zero) [23]. On the other hand, for the high-temperature behavior of the elastic constants (above room temperature up to the point where the materials cease to be purely elastic, say) no general rules can be given, although for many simple ceramics (alumina, magnesia, thoria etc.) a slightly nonlinear decrease with increasing temperature seems to be typical [16, 23]. Several relations have been proposed to fit this type of temperature dependence [19, 23].

#### Porosity dependence of elastic constants

The presence of pores generally leads to a decrease of the elastic moduli, while the influence on the Poisson ratio is highly complex and still a point of dispute [24]. The porosity dependence of elastic moduli has been treated in great detail in many previous papers [25-30], where the relevant literature references can be found. Therefore only the main results concerning the Young's modulus of porous materials with isometric pores are listed here, since only these will be used in the present context.

It has to be recalled, that in the case of porous materials the lower micromechanical bounds fail [29], and thus only the upper bounds remain intact. These are the Voigt bound (volume-weighted arithmetic mean) [31]

$$E_r = 1 - \phi, \quad (35)$$

valid for porous materials of arbitrary symmetry, and the upper Hashin-Shtrikman (HS) bound [32]

$$E_r = \frac{1 - \phi}{1 + \phi}, \quad (36)$$

valid for isotropic porous materials only. In these relations  $\phi$  is the porosity and  $E_r$  is the relative Young's modulus, defined as the ratio between the effective Young's modulus of the porous material and the Young's modulus of the solid phase.

The two upper bounds are the only guidelines available without invoking model-based predictions. The simplest and most useful model-based predictions are all based on the linear approximation (also called dilute or non-interaction approximation, in reality the exact solution of the single-inclusion problem of a spherical void in an infinite medium)

$$E_r = 1 - 2\phi, \quad (37)$$

Although the numerical coefficient is, strictly speaking, a function of the Poisson ratio of the solid phase, to a very good approximation it may be assumed to be 2 for isometric pores [29]. Based on this linear approximation, to which all admissible porosity dependence functions must reduce in the dilute limit ( $\phi \rightarrow 0$ ), the following non-linear types of relations have been proposed:

- Coble-Kingery relation (a second-order relation based on the boundary condition  $E_r = 0$  for  $\phi = 1$ ) [11, 25, 33]:

$$E_r = 1 - 2\phi + \phi^2 \quad (38),$$

- Gibson-Ashby relation (a semi-empirical power-law relation derived via a unit cell approach, strictly derivable via the differential scheme approach) [11, 26, 34, 35]:

$$E_r = (1 - \phi)^2 \quad (39),$$

- Pabst-Gregorová relation (a modified exponential relation derived via the functional equation approach) [11, 27, 28]:

$$E_r = \exp\left(\frac{-2\phi}{1 - \phi}\right) \quad (40).$$

Note that the numerical value 2 of the linear coefficient reappears in all these relations for the Young's modulus and has to be replaced by another value when other properties are considered (e.g. 3/2 for thermal conductivity) [36, 37]. Note also that, accidentally, due to the aforementioned fact that for the Young's modulus the numerical coefficient is extremely close to 2, the Coble-Kingery relation is identical to the Gibson-Ashby relation (this is true only for the Young's modulus, but not for other elastic moduli [11]) so that in effect only two of these model relations remain: the power law, Equation (39), and our exponential relation, Equation (40). All these relations reduce to the correct dilute limit, are below the Hashin-Shtrikman upper bound, as required on theoretical grounds, and are predictive in the sense that when the Young's modulus of the solid phase is known, these relations provide parameter-free

predictions of the porosity dependence of the Young's modulus. Together with the upper Hashin-Shtrikman bound, Equation (36), which also corresponds to a realizable microstructure, this is a set of three (mutually exclusive) model relations that are available for the effective Young's modulus of isotropic porous materials. However, the last of these, our exponential relation, is the lowest of these predictions and has turned out to be the most adequate relation for predicting the porosity dependence of the Young's modulus in the majority of cases (with the exception of cellular materials with porosities above 70 %) [38-40].

#### Structure and thermophysical properties of mullite and mullite ceramics

Mullite is an aluminosilicate with a variable aluminum-to-silicon ratio represented by the solid solution series  $\text{Al}_2[\text{Al}_{2+2x}\text{Si}_{2-2x}]\text{O}_{10-3x}$ , where the  $x$  value corresponds to the number of oxygen vacancies [41]. The composition of mullite observed so far is in the range  $0.18 \leq x \leq 0.88$ , corresponding to 57 - 92 mol %  $\text{Al}_2\text{O}_3$  [42], but the most important types are 3:2 mullite ( $x = 0.25$ , typical for "sinter mullite", also called "stoichiometric mullite", with alumina contents of about 60 mol % = 72 wt. %) and 2:1 mullite ( $x = 0.40$ , typical for "fused mullite", with alumina contents of about 64 mol % = 76 wt. %) [2]. Sillimanite, one of the three  $\text{Al}_2\text{SiO}_5$  polymorphs with stability regions at high pressures, has a structure similar to mullite and its disordered variant can be considered as a mullite with  $x = 0.00$  (note, however, that there is probably a miscibility gap between sillimanite and mullite [2]) while the transition alumina phase  $\gamma\text{-Al}_2\text{O}_3$  can be considered as a completely silica-free analogue of mullite with  $x = 0.00$  [43]. The unit cell parameters, and thus the density, of mullite depend on the  $\text{Al}_2\text{O}_3$  content, and thus the composition of mullites can be deduced from X-ray diffraction data [1, 2]. Structural details and their relation to mullite synthesis have been described in great detail in the literature. The interested reader may refer to [2], where the relevant references can be found.

Based on the lattice constants, or unit cell volumes, listed in [2], which have been extracted from 12 literature references, and the composition given there, the true density  $\rho_0$  of mullite at room temperature can be determined to be  $3.14 \pm 0.03 \text{ g/cm}^3$ , in good agreement with the range 3.16 - 3.22  $\text{g/cm}^3$ , commonly reported for dense mullite ceramics [1, 44]. With increasing tem-

perature the lattice constants increase and thus the density decreases, but the (linear or volumetric) coefficients of thermal expansion (CTEs) do not change very much with temperature, so that the apparent CTEs for finite temperature intervals  $\alpha_{T_1-T_2}$  should be reasonably close to the true CTEs. Averaged over all monocrystal orientations using the arithmetic mean of the (linear) CTE values  $\alpha$  for the  $a$ ,  $b$  and  $c$  axes [19], these values are between approximately  $5.3 - 5.6 \times 10^{-6} \text{ K}^{-1}$  from 300°C to 1000°C and  $7.2 - 7.5 \times 10^{-6} \text{ K}^{-1}$  above 1000°C up to 1600°C [45, 46]. These values are in good agreement with  $\alpha$  values reported for mullite and mullite ceramics elsewhere in the literature, which range from  $4.8 - 5.7 \times 10^{-6} \text{ K}^{-1}$  below 1000°C [1, 47]. However, the true  $\alpha$  values vary in a broader range because the lattice constants do not change linearly with temperature. An estimate based on the temperature dependence of the lattice constants [2] indicates true  $\alpha$  values ranging from less than  $4.0 \times 10^{-6} \text{ K}^{-1}$  at room temperature to more than  $8.0 \times 10^{-6} \text{ K}^{-1}$  at 1500°C. This is in reasonable agreement with the range of orientational values  $4 - 7 \times 10^{-6} \text{ K}^{-1}$  commonly reported for mullite-based fireclay or chamotte materials [48, 49]. At 1600°C the lattice constants  $a$ ,  $b$  and  $c$  are approximately 0.7605 nm, 0.7785 nm and 0.2915 nm, respectively [2], leading to a unit cell volume of approximately  $0.1726 \text{ nm}^3$  and a density of approximately  $3.05 \text{ g/cm}^3$ . The corresponding values for 500, 1000 and 1500°C are listed in Table 1. It can be concluded that from room temperature up to 1600°C the apparent linear CTE increases from about  $4 \times 10^{-6} \text{ K}^{-1}$  to more than  $8 \times 10^{-6} \text{ K}^{-1}$  and the density decreases from approximately  $3.14 \text{ g/cm}^3$  down to  $3.05 \text{ g/cm}^3$ .

The specific heat at constant pressure  $c_p$  of mullite is relatively well known. Figure 1 shows the temperature dependence of the specific heat for 3:2 mullite, according to the fit curve parameters from [50]. This temperature dependence is in satisfactory agreement with other literature data, although more recent research revealed a step in the heat capacity above 1000°C, possibly indicating a phase transition [51]. It is evident that the specific heat exhibits a monotonic increase and that it approaches for high temperatures the value calculated according to the Dulong-Petit rule [21] or – more precisely – the Neumann-Kopp rule [22], which is for  $c_p$  approximately

$$c_p = 26.8 \cdot (n/m) , \quad (41)$$

(in  $\text{J}/(\text{gK})$ ); for  $c_V$  the numerical constant would be 25.1 [21]), where  $n$  is the number of elements in a formula

Table 1. Orientational values for the true density, true thermal expansion coefficient and specific heat at constant pressure for mullite (dense isotropic polycrystalline materials).

Temperature (°C)	Density ( $\text{g/cm}^3$ )	CTE ( $10^{-6} \text{ K}^{-1}$ )	Specific heat ( $\text{J/gK}$ )	Bulk modulus (GPa)
25	3.14	4.0	0.598	170.9
500	3.13	6.0	1.155	162.8
1000	3.10	7.5	1.253	154.2
1500	3.06	8.0	1.310	145.7

unit (= 21 for ideal stoichiometric 3:2 mullite with the formula  $3 \text{Al}_2\text{O}_3 \times 2 \text{SiO}_2 = \text{Al}_6\text{Si}_2\text{O}_{13}$ ) and  $m$  is the molar mass (=  $3 \times 102 \text{ g/mol}$  for  $\text{Al}_2\text{O}_3$  and  $2 \times 60.1 \text{ g/mol}$  for  $\text{SiO}_2$ , i.e.  $426.2 \text{ g/mol}$  for 3:2 mullite totally). According to this rule the asymptotic value for 3:2 mullite is  $1.32 \text{ J/(gK)}$ .

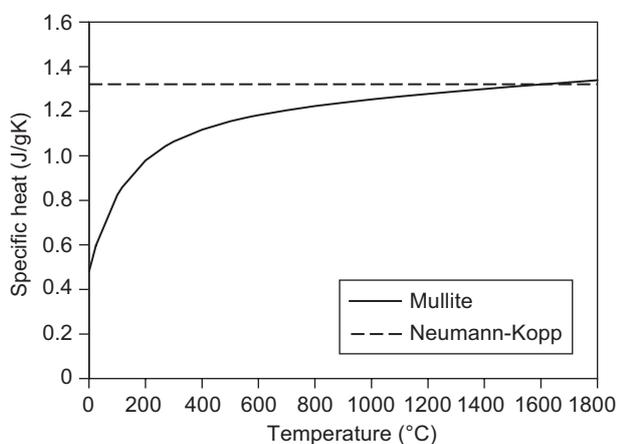


Figure 1. Temperature dependence of the specific heat at constant pressure for mullite (based on the fit parameters listed in [50]).

Table 1 summarizes the recommended orientational values of the true density  $\rho_0$ , the true coefficient of thermal expansion  $\alpha$  and the specific heat at constant pressure  $c_p$  for mullite at selected temperatures in the range from room temperature up to  $1500^\circ\text{C}$ . All these values are needed, in addition to the bulk modulus, to estimate the difference between isothermal and adiabatic elastic constants, which are measured via static and dynamic methods, respectively.

Table 1 also lists the estimated bulk moduli for the temperatures in question. The bulk moduli listed there are based on the adiabatic value  $170.9 \text{ GPa}$  at room temperature (see Table 3 below) and have been calculated assuming a linear decrease of  $1 \times 10^{-4} \text{ K}^{-1}$ , i.e. the a decrease by  $0.00878 \text{ GPa}$  ( $0.01 \%$  of the initial room temperature value) per Kelvin. Such a decrease is certainly the correct order of magnitude and relatively close to reality, since (negative slope) temperature coefficients in the range  $0.7 - 1.2 \times 10^{-4} \text{ K}^{-1}$  can be read off from the temperature dependence of stiffness constants in [2] and similar values,  $0.5 - 0.9 \times 10^{-4} \text{ K}^{-1}$ , have been reported for the temperature dependence of the Young's modulus [4, 52].

The symmetry (crystal system) of mullite is orthorhombic (point group  $mmm$ , space group  $Pbam$ ), although accidentally pseudotetragonal variants may occur (when  $a = b$  at a certain composition) [2]. That means, mullite single crystals have, in general, nine independent elastic constants (stiffnesses) or elastic coefficients (compliances) [10].

#### Elastic properties of mullite and mullite ceramics

Table 2 lists the elastic constants (stiffnesses) reported in the literature for mullite at room temperature. These values have been measured by dynamic methods (Brillouin spectroscopy [5, 6] and resonant ultrasound spectroscopy [7, 8]) for mullite single crystals of density  $3.11 \pm 0.01 \text{ g/cm}^3$  and thus represent adiabatic elastic constants. The corresponding values for sillimanite [53] are given for comparison.

Table 2. Components of the elasticity tensor (stiffness matrix) for mullite and sillimanite single crystals at room temperature (all values in [GPa]).

Phase	$C_{11}$	$C_{22}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$	$C_{12}$	$C_{23}$	$C_{31}$	Ref.
2.5:1 mullite	280.0	245.0	362.0	111.0	78.1	79.0	105.0	135.0	99.2	[5]
2.5:1 mullite	281.9	244.2	363.6	111.7	78.2	79.2	105.1	142.3	100.3	[6]
2:1 mullite	291.3	232.9	352.1	110.3	77.39	79.9	112.9	121.9	96.2	[7]
2:1 mullite	279.5	234.9	360.6	109.5	74.94	79.9	103.1	135.6	96.1	[8]
Sillimanite	287.3	231.9	388.4	122.4	80.7	89.3	94.7	158.6	83.4	[53]

Table 3. Components of the elasticity tensor for mullite (and sillimanite) single crystals at room temperature.

Phase	$E_V$	$E_R$	$E_{VRH}$	$G_V$	$G_R$	$G_{VRH}$	$K_V$	$K_R$	$K_{VRH}$	Poisson ratio
	(GPa)									
2.5 : 1 mullite [5]	230.6	222.0	226.3	90.1	86.6	88.4	173.9	169.4	171.7	0.280
2.5 : 1 mullite [6]	230.6	221.2	225.9	90.0	86.1	88.0	176.1	171.0	173.6	0.283
2 : 1 mullite [7]	229.4	220.0	224.7	89.9	85.9	87.9	170.9	167.5	169.2	0.279
2 : 1 mullite, optimized [7]	–	–	224.7	–	–	87.86	–	–	169.2	0.2787
2 : 1 mullite [8]	227.4	217.5	222.4	88.9	84.8	86.8	171.6	166.5	169.0	0.281
Sillimanite [9]	244.8	227.1	236.0	96.5	89.2	92.9	175.7	167.1	171.4	0.2705
Average mullite, without optimization	–	–	224.8	–	–	87.8	–	–	170.9	0.281
Average mullite, optimized	–	–	224.89	–	–	87.80	–	–	170.91	0.2807

Table 3 lists the effective elastic constants calculated from the monocrystal data in Table 2, including the optimized data sets (involving changes in the second decimal). Obviously, the differences between 2.5:1 and 2:1 mullite are quite small. Unfortunately, monocrystal data for 3:2 (= 1.5:1) mullite are not available. At first sight it seems, that there is a trend to lower elastic moduli when going from 2.5:1 to 2:1 mullite, and it might be tempting to “extrapolate” this trend to a 1.5:1 (= 3:2) mullite. The comparison with sillimanite ( $\approx$  1:1 mullite), however, may be taken as evidence for the fact that no such trend exists and that any attempts to deduce the elastic constants of 3:2 mullite by this kind of “extrapolation” must be futile. Therefore, at the current state of the art, the differences between the data sets must be attributed to experimental scatter, not indicating typical differences between specific compositional variants of mullite. Therefore it is probably justified to consider the average values of the four data sets as the most reliable elastic constants.

Table 4 lists the corresponding average relative RMS deviations before and after optimization. It is evident that before optimization the average data set exhibits a similar degree of mutual consistency as the individual data sets. However, the optimization results show, that this consistency can be greatly improved by changing the calculated averages by less than 0.1 GPa (which is hardly measurable). Actually, after optimization the average set of elastic constants (obtained in this work by averaging the VRH averages of four reliably known monocrystal data sets) has the highest degree of consistency and can thus be considered as a very reliable data set for mullite. These are the data that can be compared with the (porosity-corrected) data measured for mullite ceramics

[1, 2, 4, 54, 55] and recommended as input data for the calculation of mullite-containing multiphase ceramics (e.g. porcelain, fireclay refractories) and composites (e.g. mullite-zirconia composites, high-alumina refractories).

It has to be emphasized that all these values refer to adiabatic elastic constants. In order to obtain estimates of the expected isothermal elastic constants, the  $c_p/c_T$  ratios may be calculated using the thermomechanical data from Tables 1 and 3. Table 5 shows the results of these calculations.

It is evident that the relative differences between adiabatic and isothermal elastic constants increase slightly with temperature, but remain below 4 % and 2.5 % for the bulk modulus and Poisson ratio. Apart from the shear moduli, for which they are identically zero, the relative differences are lowest for the Young’s modulus, and remain below 0.5 % even at 1500°C. That means, the difference between the adiabatic and isothermal Young’s moduli of mullite will be hardly detectable by routine measurement techniques, and thus can be neglected in practice.

## CONCLUSION

In this first part of a two-paper set on the elastic properties of mullite and mullite-containing ceramics the current literature has been reviewed and, based on the available monocrystal data, a mutually consistent average set of elastic constants for dense polycrystalline mullite materials at room temperature has been calculated and optimized via minimization of the total average relative root mean square (RMS) deviation. Based on the results of this paper, the recommended

Table 4. Average relative RMS deviations for the individual elastic constants ( $E, G, K, \nu$ ) and total average relative RMS deviation for all elastic constants (all values in  $10^{-5}$ ).

Data set and reference	$\Delta_E$	$\Delta_G$	$\Delta_K$	$\Delta_\nu$	$\Delta$
2.5 : 1 mullite [5]	59.2	60.0	154.6	76.0	87.4
2.5 : 1 mullite [6]	41.2	56.3	112.8	97.2	76.9
2 : 1 mullite [7]	83.8	107.7	199.5	189.9	145.2
2 : 1 mullite, optimized [7]	8.1	7.3	21.0	11.9	12.1
2 : 1 mullite [8]	62.5	61.4	163.8	83.2	92.7
Average mullite, without optimization	69.5	93.0	180.7	162.1	126.3
Average mullite, optimized	1.1	1.3	2.3	2.1	1.7

Table 5. Calculated ratios between adiabatic and isothermal bulk moduli ( $= c_p/c_T$  ratios) of mullite, their relative differences as well as the corresponding ratios and differences for Young’s moduli and Poisson ratios at room temperature, 500, 1000 and 1500°C.

Temperature (°C)	$c_p/c_T = \tilde{K}/K$	Relative difference		Relative difference	
		$(\tilde{K} - K)/K$ (%)	$\tilde{E}/E$	$(\tilde{E} - E)/E$ (%)	$\tilde{\nu}/\nu$
25°C	1.0039	0.4	1.00057	0.1	1.00374
500°C	1.0113	1.1	1.00165	0.2	1.00757
1000°C	1.0256	2.6	1.00374	0.4	1.01730
1500°C	1.0371	3.7	1.00543	0.5	1.02525

values of adiabatic elastic constants are 224.9 GPa for the Young's modulus, 87.8 GPa for the shear modulus, 170.9 GPa for the bulk modulus and 0.281 for the Poisson ratio. The RMS deviation of this set is lower than for any other set, and thus these values exhibit a high degree of mutual consistency with respect to the elasticity standard relations. Micromechanical upper bounds and model relations have been summarized for describing the porosity dependence of elastic moduli, and a simple relation has been used to estimate the difference between adiabatic and isothermal elastic constants. The results show that this difference increases slightly with temperature, but is not larger than 4 % even at 1500°C. In particular, for the Young's modulus the difference remains below 0.5 %. That means, the difference between adiabatic and isothermal Young's moduli will usually be unmeasurably small and negligible in practice.

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