EFFECTIVE ELASTIC PROPERTIES OF ALUMINA-ZIRCONIA COMPOSITE CERAMICS - PART 3. CALCULATION OF ELASTIC MODULI OF POLYCRYSTALLINE ALUMINA AND ZIRCONIA FROM MONOCRYSTAL DATA

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In this third paper of a series on the effective elastic properties of alumina-zirconia composite ceramics the calculation of the effective elastic moduli of polycrystalline alumina (corundum, i.e. trigonal α-Al_2O_3) and tetragonal zirconia (t-ZrO_2) from monocrystal data is recalled. The values estimated via the Voigt-Reuss-Hill average are compared with the most reliable published values. Standard formulae and theorems of elasticity theory and micromechanics are used as consistency tests for calculated and measured values. For dense polycrystalline α- Al_2O_3 the most reliable values calculated from monocrystal data are 402.7 GPa for the tensile modulus, 163.4 GPa for the shear modulus, 250.9 GPa for the bulk modulus and 0.23 for the Poisson ratio. In this case all the calculated values are in reasonable agreement with the measured values, taking into account the relatively large statistical errors of the latter. For dense polycrystalline zirconia values calculated from monocrystal data are 201.1 GPa for the tensile modulus, 78.7 GPa for the shear modulus, 150.6 GPa for the bulk modulus and 0.28 for the Poisson ratio. There is a discrepancy between calculated and measured values, especially for the bulk modulus, the measured values of which are approx. 180 ± 10 GPa and the Poisson ratio, the measured values of which are approx. 0.31. Possible reasons of this discrepancy are discussed.

INTRODUCTION

In Parts 1 and 2 of this series of papers, the linear theory of elasticity has been summarized for anisotropic and isotropic materials [1] and the fundamentals of micromechanical modeling have been reviewed [2]. In the present paper the reader is assumed to be familiar with the contents of these preceding parts and the notation introduced there. Now we use standard micromechanical relations for the calculation of the effective elastic constants of statistically isotropic polycrystalline ceramics (alumina and zirconia) from the values measured for the components of the elasticity tensor of alumina and zirconia monocrystals. For this calculation we use the best values of the components of the stiffness and compliance matrix, respectively, avaliable in the literature for alumina and zirconia monocrystals. In the case of statistically isotropic ("quasi-isotropic") polycrystalline materials consisting of randomly oriented monocrystals usually the Voigt and Reuss bounds are sufficiently close, so that there is no need to apply more complex bounds, e.g. of Hashin-Shtrikman type, in order to achieve a realistic estimate of the effective elastic properties. In this sense, we calculate the Voigt and Reuss bounds and, following a suggestion of Hill [3], take the arithmetic average of these bounds (the so-called "Voigt-Reuss-Hill average") as the most reliable estimate. The calculated values are compared with measured values available in the literature and in electronic databases.

THEORETICAL

Alumina and Zirconia – Monocrystals and Polycrystalline Materials

Throughout this paper, by "alumina" we mean monocrystals or polycrystalline aggregates of the pure α-phase of Al_2O_3 (mineral name: corundum, sometimes termed sapphire after the blue gemstone variety of corundum), which is thermodynamically stable at room temperature and exhibits trigonal (rhombohedric) symmetry (space group $R\bar{3}c$, i.e. point group/crystal class $\bar{3}m$). By "zirconia" we mean the tetragonal phase of ZrO_2 (t-ZrO_2) with space group $P4_2/n\ mc$, i.e. point group/crystal class 4/*mmm*, cf. e.g. [4]. As detailed in Part 1 of this series of papers [1], the elastic behavior of all trigonal and tetragonal monocrystals is fully described by 6 independent elastic constants (stiffnesses). The measurement of monocrystal elastic constants (stiffnesses) is usually performed by measuring X-ray or neutron diffraction on mechanically loaded or vibrating specimens [5-12]. Since the tetragonal phase of pure ZrO_2 is unstable at room temperature, tetragonal ZrO_2 monocrystals of macroscopic size are not available and even micron- and submicron-sized zirconia has to be doped with additives (built into the zirconia lattice) in order to retain the tetragonal phase at least in the bulk of polycrystalline aggregates (e.g. sintered ceramics). Today the most frequent compositions applied to retain the tetragonal phase after sintering down to room temperature (given a sufficiently small grain size[1] depending on the grain shape and other factors [4,13,14]) are zirconia compositions with 3 mol.% yttria (Y_2O_3) or with 12 mol.% ceria (CeO_2). Of course, under suitable conditions, e.g. stresses generated at the tip of a propagating crack, even these doped tetragonal grains transform (via a martensitic mechanism) to the monoclinic phase of ZrO_2. When duely controlled, it is just this effect which can be exploited to enhance the strength and fracture toughness of zirconia and zirconia-containing composites (transformation toughening) [15]. The non-availability of t-ZrO_2 monocrystals of macroscopic size is the reason why there are no unbiased monocrystal data in the literature. Nevertheless, it is possible to infer the elastic constants of t-ZrO_2 monocrystals from diffraction measurements on polycrystalline samples when these measurements are supplemented (calibrated) by an independent strain gauge measurement on the polycrystalline specimen and an ad hoc assumption concerning the interpretation of the results of this independent measurement. While Wachtman et al. [5] performed classical X-ray diffraction measurements on mechanically vibrating alumina monocrystals (dynamic measurement), Kisi and Howard [10] used neutron diffraction on a mechanically loaded specimen (static measurement) and measured a tensile modulus of 192 GPa for a polycrystalline t-ZrO_2 specimen containing 12 mol.% CeO_2. Based on previous experience with cubic zirconia in the same experimental array [11], they considered this value as being close to the Reuss bound [10].[2] With this additional information at hand, they succeeded in determining all 6 elasticity constants (stiffnesses) from their neutron diffraction results. As soon as the monocrystal data (6 stiffnesses and 6 compliances) are known, it is possible to predict the 2 elastic constants, necessary for a complete description of the elastic behavior of dense (i.e. non-porous), statistically isotropic (quasi-isotropic)[3] polycrystalline aggregates, as the Voigt-Reuss-Hill average from these data. The calculation of these 2 elastic constants is recalled in this paper and its results compared to published data measured on polycrystalline specimens. In the next section the necessary standard formulae and theorems of elasticity theory and micromechanics are briefly summarized to the extent indispensable for the following calculations.

Formulae and theorems of elasticity theory and micromechanics

As detailed in Part 1 of this series, all trigonal and tetragonal monocrystals can be described by 6 independent elastic constants [1]. The stiffness matrix of trigonal monocrystals is

$$[C_{\mathrm{trigonal}}] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{21} & C_{22} & C_{23} & C_{24} & 0 & 0 \\ C_{31} & C_{32} & C_{33} & 0 & 0 & 0 \\ C_{41} & C_{42} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & C_{56} \\ 0 & 0 & 0 & 0 & C_{65} & C_{66} \end{bmatrix} \tag{1}$$

with the conditions $C_{ij} = C_{ji}$ (diagonal symmetry),

$$C_{11} = C_{22}\,,\ C_{13} = C_{23}\,,\ C_{44} = C_{55} \tag{2}$$

and

$$C_{14} = -C_{24} = C_{56}\,,\ C_{66} = ½(C_{11} - C_{12}) \tag{3}$$

For tetragonal monocrystals the stiffness matrix is

$$[C_{\mathrm{tetragonal}}] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{21} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{31} & C_{32} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \tag{4}$$

together with conditions $C_{ij} = C_{ji}$ (diagonal symmetry) and (2). Based on the knowledge of the stiffness matrix alone, the Voigt bound (upper bound) of the polycrystalline elastic properties can be calculated. In order to calculate the Reuss bound (lower bound), the compliance matrices $[S]$, i.e. the inverses of the siffness matrices $[C] = [S]^{-1}$, must be known additionally [2,13,16-18].

For trigonal monocrystals the following inversion relations hold:

$$S_{11} + S_{12} = \frac{C_{33}}{K}\,,\ S_{11} - S_{12} = \frac{C_{44}}{K'}\,,\ S_{13} = -\frac{C_{13}}{K}\,, \tag{5a,b,c}$$

$$S_{14} = \frac{C_{14}}{K'}\,,\ S_{33} = \frac{C_{11} + C_{12}}{K}\,,\ S_{44} = \frac{C_{11} - C_{12}}{K'}\,. \tag{5d,e,f}$$

The inversion relations for tetragonal monocrystals are:

$$S_{11} + S_{12} = \frac{C_{33}}{K}\,,\ S_{11} - S_{12} = \frac{1}{C_{11} - C_{12}}\,,\ S_{13} = -\frac{C_{13}}{K}\,, \tag{6a,b,c}$$

$$S_{33} = \frac{C_{11} + C_{12}}{K}\,,\ S_{44} = \frac{1}{C_{44}}\,,\ S_{66} = \frac{1}{C_{66}}\,. \tag{6d,e,f}$$

In these relations K and K' have the following meaning:

$$K = C_{33}(C_{11} + C_{12}) - 2C_{13}^2 , \tag{7}$$

$$K' = C_{44}(C_{11} - C_{12}) - 2C_{14}^2 . \tag{8}$$

Totally analogous relations are valid with the stiffnesses C_{ij} interchanged by the compliances S_{ij}, with one exception: for trigonal crystals

$$S_{66} = 2\,(S_{11} - S_{12}) \tag{9}$$

cf. equation (3c). Statistically isotropic ("quasi-isotropic") polycrystalline materials are (macroscopically) fully characterized by two independent (effective) elastic constants. For these materials the stiffness matrix has the general form (4) with the conditions

$$\begin{gathered} C_{11} = C_{22} = C_{33}\,,\; C_{12} = C_{23} = C_{31}\,, \\ C_{44} = C_{55} = C_{66} = ½(C_{11} - C_{12}) \end{gathered} \tag{10}$$

i.e. the stiffness matrix can be written in terms of the Lamé constants, or alternatively, using either of the pair of elastic constants (moduli) E (tensile modulus), G (shear modulus), K (bulk modulus) and ν (Poisson ratio), cf. [1,13,18]. Since only two of these are independent, the remaining ones can be calculated as soon as two are known, cf. e.g. Table 1 in Part 1 of this series of papers [1]. The most important relations can be summarized as follows:

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) = \frac{9KG}{3K + G} \tag{11}$$

$$G = \frac{E}{2(1 + \nu)} = \frac{3K(1 - 2\nu)}{2(1 + \nu)} = \frac{3EK}{9K - E} \tag{12}$$

$$K = \frac{E}{3(1 - 2\nu)} = \frac{2G(1 + \nu)}{3(1 - 2\nu)} = \frac{EG}{3(3G - E)} \tag{13}$$

$$\nu = \frac{E - 2G}{2G} = \frac{3K - 2G}{2(3K + G)} = \frac{3K - E}{6K} \tag{14}$$

It is clear that consistent monocrystal data must obey the inversion relations, equations (5) and (6), exactly. Similarly, in order to provide a consistent set of elastic constants (moduli), the effective elastic moduli of quasi-isotropic polycrystalline materials, whether calculated or measured, should satisfy the standard elasticity relations for isotropic materials, equations (11) through (14), at least approximately.

According to Voigt [19,20] the effective tensile modulus of a polycrystalline material is

$$E_V = \frac{(A - B + 3C)(A + 2B)}{2A + 3B + C} \tag{15}$$

the effective shear modulus

$$G_V = \frac{A - B + 3C}{5} \tag{16}$$

and the effective bulk modulus

$$K_V = \frac{A + 2B}{3} \tag{17}$$

In these expressions A, B, C are given by

$$A = \frac{C_{11} + C_{22} + C_{33}}{3} \tag{18}$$

$$B = \frac{C_{12} + C_{23} + C_{31}}{3} \tag{19}$$

$$C = \frac{C_{44} + C_{55} + C_{66}}{3} \tag{20}$$

According to Reuss [21] the effective tensile modulus of a polycrystalline material is

$$E_R = \frac{5}{3X + 2Y + Z} \tag{21}$$

the effective shear modulus

$$G_R = \frac{5}{4X - 4Y + 3Z} \tag{22}$$

and the effective bulk modulus

$$K_R = \frac{1}{3(X + 2Y)} \tag{23}$$

In these expressions X, Y, Z are given by

$$X = \frac{S_{11} + S_{22} + S_{33}}{3} \tag{24}$$

$$Y = \frac{S_{12} + S_{23} + S_{31}}{3} \tag{25}$$

$$Z = \frac{S_{44} + S_{55} + S_{66}}{3} \tag{26}$$

Hill [3] has shown that the Voigt values are the upper bound and the Reuss values the lower bound of the effective elastic moduli of statistically isotropic polycrystalline materials, i.e.

$$M_R \leq M \leq M_V \tag{27}$$

with M = E, G, K, respectively (Hill's theorem). Following Hill's suggestion, we use the arithmetic average[4] of the Voigt and the Reuss value as an estimate (prediction) for the respective effective elastic modulus ("Voigt-Reuss-Hill average", abbreviated "VRH-average"), i.e.

$$M_{VRH} = \frac{M_V + M_R}{2} \tag{28}$$

Estimates (predictions) of the effective Poisson ratio of statistically isotropic polycrystalline materials can be given using E_V, G_V, K_V, or E_R, G_R, K_R, or the corresponding VRH averages, in the standard formula (14). It has to be noted, however, that the Poisson ratio has several exceptional properties, which are well known in elasticity theory. In particular, the effective Poisson ratio cannot be expected a priori to satisfy the Voigt-Reuss bounds, cf. [22]. Note in passing that in the case of trigonal crystals, such as alumina, only five of the six independent elastic constants or coefficients (i.e. stiffnesses or compliances) are necessary for calculating the effective elastic properties (moduli and Poisson ratio) of the corresponding polycrystalline materials.

CALCULATION OF EFFECTIVE ELASTIC PROPERTIES

Tables 1 through 4 list the elastic constants (stiffnesses) and elastic coefficients (compliances) determined for alumina and zirconia. Note that the values for alumina are measured on monocrystals (X-ray diffraction) [5-9], while the values for zirconia are inferred from measurements on polycrystalline materials (neutron diffraction) [10], since t-ZrO_2 monocrystals are not available (see the discussion above).

Table 1. Elastic constants (siffnesses, i.e. elements of the stiffness matrix [C]) for trigonal alumina monocrystals according to Wachtman et al. [5], Sundara-Rao [6], Bhimasenachar [7] and Mayer & Hiedemann [8,9].

C_{ij} (GPa)	Wachtman et al.	Sundara-Rao (original)	Bhimasenachar	Mayer & Hiedemann
C_{11}	496.8 ± 1.8	466	465	496
C_{33}	498.1 ± 1.4	506	563	502
C_{44}	147.4 ± 0.2	235	233	206
C_{12}	163.6 ± 1.8	127	124	109
C_{13}	110.9 ± 2.2	117	117	48
C_{14}	– 23.5 ± 0.3	94	101	38
C_{66} (calc.)	166.6	169.5	170.5	193.5

A more detailed inspection of tables 1 and 2 reveals that Bhimasenachar's values [7] for alumina do not satisfy the inversion relations (5), i.e. either (some of) the stiffnesses or (some of) the compliances are in error. Similarly, Sundara-Rao's original values [6] are not fully consistent, probably due to a misprint. These values can be made consistent, however, by replacing the value -0.00047 of the compliance S_{13} by the value -0.00043, calculated according to the inversion relation (5c), cf. the fourth column (labelled "corrected") in table 2. Table 5 lists the effective elastic properties of polycrystalline alumina, calculated according to relations (15) through (26), from the available monocrystal data. It is evident that the Voigt and Reuss bulk modu-

Table 3. Elastic constants (siffnesses, i.e. elements of the stiffness matrix [C]) for tetragonal zirconia according to Kisi & Howard [10] and Chan [12] (cited in [10]).

C_{ij} (GPa)	Kisi & Howard	Chan (original)
C_{11}	327	263
C_{33}	264	262
C_{44}	59	55.9
C_{12}	100	15
C_{13}	62	72
C_{14}	–	–
C_{66}	64	44

Table 4. Elastic coefficients (compliances, i.e. elements of the compliance matrix [S]) for tetragonal zirconia according to Kisi & Howard [10] and Chan [12] (cited in [10]).

C_{ij} (GPa^{-1})	Kisi & Howard	Chan (original)	Chan (corrected)
S_{11}	0.00346	0.00412	0.00412
S_{33}	0.00406	0.00445	0.00445
S_{44}	0.0170	0.0179	0.0179
S_{12}	– 0.00096	0.00034	0.000081
S_{13}	– 0.00059	– 0.00115	– 0.00115
S_{14}	–	–	–
S_{66}	0.0154	0.00568	0.0227

Table 2. Elastic coefficients (compliances, i.e. elements of the compliance matrix [S]) for trigonal alumina monocrystals according to Wachtman et al. [5], Sundara-Rao [6], Bhimasenachar [7] and Mayer & Hiedemann [8,9] (in brackets ± the incertainty of the last digit).

S_{ij} (GPa^{-1})	Wachtman et al.	Sundara-Rao (original)	Sundara-Rao (corrected)	Bhimasenachar	Mayer & Hiedemann
S_{11}	0.002353 (2)	0.00284	0.00284	0.00232	0.00218
S_{33}	0.002170 (2)	0.00221	0.00221	0.00193	0.00202
S_{44}	0.006940 (8)	0.00547	0.00547	0.00577	0.00504
S_{12}	– 0.000716 (7)	– 0.00095	– 0.00095	– 0.00105	– 0.00050
S_{13}	– 0.000364 (6)	– 0.00047	– 0.00043	– 0.00038	– 0.00016
S_{14}	0.000489 (5)	– 0.00152	– 0.00152	– 0.00171	– 0.00049
S_{66} (calc.)	0.003274	0.00758	0.00758	0.00674	0.00536

lus values calculated with Bhimasenachar's and Sundara-Rao's original data violate Hill's theorem, equation (27), because the Voigt values are smaller than the Reuss values. For this reason they have to be discarded.

Similarly, inspection of tables 3 and 4 reveals that Chan's original values for zirconia, which are known only from Kisi & Howard's paper [10] as a private communication [12], do not satisfy the inversion relations (6). And again, Hill's theorem, equation (27), is violated in this case, because the Voigt values are smaller than the Reuss values for the tensile modulus and the bulk modulus. Thus, for the same reason as above they have to be discarded as well.[5] Table 6 lists the effective elastic properties of polycrystalline zirconia, calculated according to relations (15) through (26), from the available monocrystal data.

For both alumina and zirconia the effective Poisson ratios ν, calculated via relation (14) using the Voigt and Reuss values, respectively, of the elastic moduli, are in generally not upper (Voigt) and lower (Reuss) bounds. This indicates that for the Poisson ratio the Voigt and Reuss bounds are not valid in general.

Table 7 lists the Voigt-Reuss-Hill averages calculated on the basis of the remaining, fully consistent, monocrystal data sets. All these sets satisfy approximately the elasticity standard relations.

Table 6. Effective elastic properties (moduli and Poisson ratio) of polycrystalline zirconia (dense, quasi-isotropic), calculated from the data of Kisi & Howard [10] and Chan [12] (cited in [10]).

Effective elastic property	Kisi & Howard	Chan (original)	Chan (corrected)
E_V	209.9	183.0	183.0
E_R	192.2	198.3	162.8
G_V	82.7	73.1	73.1
G_R	74.7	81.9	63.8
K_V	151.8	122.9	122.9
K_R	149.3	114.0	121.2
ν *	0.270 – 0.285	0.252 – 0.210	0.252 – 0.276

* The first value is the effective Poisson ratio calculated via relation (14) using the Voigt values of the elastic moduli, the second using the Reuss values. Note that the effective Poisson ratio calculated from the Voigt values need not be an upper bound. This indicates that for the Poisson ratio the Voigt and Reuss bounds do not hold. For this reason the indices "V" and "R" are not used for the Poisson ratio and only a range is given here.

Table 5. Effective elastic properties (moduli and Poisson ratio) of polycrystalline alumina (dense, quasi-isotropic), calculated from the monocrystal data of Wachtman et al. [5], Sundara-Rao [6], Bhimasenachar [7] and Mayer & Hiedemann [8,9].

Effective elastic property	Wachtman et al.	Sundara-Rao (original)	Sundara-Rao (corrected)	Bhimasenachar	Mayer & Hiedemann
E_V	408.2	469.0	469.0	477.3	468.3
E_R	397.1	390.5	388.9	436.4	455.4
G_V	166.0	199.7	199.7	203.0	207.0
G_R	160.7	158.4	159.0	169.8	199.7
K_V	251.4	240	240	245.4	211.6
K_R	250.4	243.3	234.2	339.0	211.0
ν *	0.229 – 0.236	0.174 – 0.232	0.174 – 0.223	0.176 – 0.285	0.131 – 0.140

* The first value is the effective Poisson ratio calculated via relation (14) using the Voigt values of the elastic moduli, the second using the Reuss values. Note that the effective Poisson ratio calculated from the Voigt values need not be an upper bound. This indicates that for the Poisson ratio the Voigt and Reuss bounds do not hold. For this reason the indices "V" and "R" are not used for the Poisson ratio and only a range is given here.

Table 7. Voigt-Reuss-Hill averages of the effective elastic properties (moduli and Poisson ratio) of polycrystalline (dense, quasi-isotropic) alumina and zirconia, calculated from the data of Wachtman et al. [5] (original), Sundara-Rao [6] (corrected), Mayer & Hiedemann [8,9] (original), Kisi & Howard [10] (original) and Chan [12] (corrected).

	Alumina			Zirconia	
Effective elastic property	Wachtman et al.	Sundara-Rao (corrected)	Mayer & Hiedemann	Kisi & Howard	Chan (corrected)
E_{VRH}	402.7	429.0	461.9	201.1	172.9
G_{VRH}	163.4	179.4	203.4	78.7	68.5
K_{VRH}	250.9	237.1	211.3	150.6	122.1
ν	0.233	0.199	0.136	0.278	0.264

COMPARISON WITH PUBLISHED DATA AND DISCUSSION

There is an enormous amount of published data on the (effective) elastic properties of polycrystalline alumina and zirconia and this paper does not intend to give a comprehensive review of these. The selection of significant data must take into account the fact that even in original papers it is not always clear, whether the data have been actually measured or whether the authors only cite "typical" values. Moreover, the method of measurement is not always specified to a sufficient degree.[6] In this paper we confine ourselves to data which have been measured by precisely specified methods (static or dynamic). Naturally, the data selection must take into account the dependence of the elastic moduli on temperature and porosity.[7] Here we confine ourselves to values measured at room temperature (25 ± 3° C) on densely sintered polycrystalline samples with a total porosity below 3 %. Assuming the theoretical (X-ray) density of alumina (α-Al_2O_3) as 4.0 g/cm^3 and that of zirconia (t-ZrO_2) as 6.1 g/cm^3, our requirement of porosity < 3 % means, that we take into account only effective elastic property values for specimens with a bulk density of at least 3.88 g/cm^3 and 5.92 g/cm^3, for alumina and zirconia, respectively.

Table 8 lists some of the most reliable data selected according to these criteria. Except for Lang's results [23] (second column, values for K and ν calculated from the measured values E and G via the elasticity standard relations (13) and (14)), all values, including Munro's [24], occur in the 2002 NIST databases [25-29]. In the case of alumina, it is evident that – within statistical errors of measurement – the agreement between calculated and experimentally measured values is generally good for the VRH-averages calculated on the basis of the monocrystal data of Wachtman et al. [5], while the VRH-averages calculated on the basis of the monocrystal data of Sundara-Rao [6] (corrected) and Mayer & Hiedemann [8,9] are too high for E and G and too low for K and ν. This is one of the reasons why the monocrystal data of Wachtman et al. have to be considered as the most reliable ones.

In the case of zirconia the calculated VRH-averages (cf. table 7, fifth and sixth column) are values for t-ZrO_2 with 12 mol.% CeO_2 and should therefore be compared in the first place with the values in last column in table 8. The agreement with the calculated VRH-averages (table 7, fifth and sixth column) is generally poor for K and ν. In the case of E and G, the VRH-averages calculated on the basis of the monocrystal data of Kisi & Howard [10] agree well with the measured values and have therefore to be considered as more reliable than Chan's values [12]. The reason for the generally poor agreement for K and ν in the case of zirconia is not quite clear. In any case, the statements that the measured K and ν values are higher than the predicted ones are physically consistent and both are indicative of the fact that polycrystalline zirconia is less compressible than it would appear from monocrystal data. This might in some way be related to the capacity of zirconia to undergo – to a certain degree – plastic deformation, a

Table 8. Measured values of the effective elastic properties (moduli and Poisson ratio) of polycrystalline (dense, quasi-isotropic) alumina and zirconia, taken from or averaged from literature data [23-29].

	Alumina			Zirconia	
Effective elastic property	Lang	Munro	NIST (Munro)	NIST (t-ZrO_2 with 3 mol.% Y_2O_3)	NIST (t-ZrO_2 with 12 mol.% CeO_2)
E	401.2	416 ± 30	392 ± 19	210 ± 6	195
G	159.1	169 ± 10	161 ± 4	81 ± 2	74
K	279.6	257 ± 50	247 ± 16	190 ± 11	180
ν	0.261	0.231 ± 0.001	0.221 ± 0.025	0.31 ± 0.01	0.32

Table 9. Recommended approximate estimates for the effective elastic properties (moduli and Poisson ratio) of polycrystalline (dense, quasi-isotropic) alumina and zirconia (G and K calculated from E and ν).

Effective elastic property	Alumina	Zirconia		
		with 3 mol% Y_2O_3	with 12 mol% CeO_2	(unspecified)
E	400	210	200	205
G	163	80	76	78
K	247	184	175	180
ν	0.23	0.31	0.32	0.31

fact that lead Kisi & Howard to the isostress (Reuss) assumption in the interpretation of their strain gauge measurement [10,11]. On the basis of the measured values available for polycrystalline ceramics, it appears that the elastic moduli of t-ZrO_2 with 3 mol.% Y_2O_3 are slightly higher that those of t-ZrO_2 with 12 mol.% CeO_2, while the Poisson ratio is the same.

When approximate estimates for the effective elastic properties are required, either for orientational purposes or as an input information for the prediction of the effective elastic properties of dense, statistically isotropic alumina-zirconia composites, we recommend the values E = 400 GPa and ν = 0.23 for alumina and E = 205 GPa and ν = 0.31 for zirconia.[8] This recommendation seems to be in agreement with the opinion of Green [18]. The corresponding values for G and K, calculated from these values via the elasticity standard relations (12) and (13), are listed in table 9.

CONCLUSIONS

The calculation of the effective elastic moduli of polycrystalline trigonal alumina (α-Al_2O_3) and tetragonal zirconia (t-ZrO_2) from the monocrystal data available in the literature has been recalled. The values estimated via the Voigt-Reuss-Hill average (VRH-average) have been compared with the most reliable measured values, primarily from the 2002 NIST databases. Using standard formulae and theorems of elasticity theory and micromechanics as consistency tests for calculated and measured values, it has been shown that certain sets of monocrystal data have to be discarded simply for reasons of consistency. It has also been shown, however, that even VRH-averages calculated from consistent data sets (monocrystal data sets satisfying the inversion relations (5), (6) and polycrystalline data satisfying Hill's theorem, equation (27), and the standard elasticity relations (11) through (14)), need not be in good agreement with experimentally measured values. In this sense, agreement with values experimentally measured on polycrystalline specimens provides an additional criterion for the reliability of monocrystal data. In view of this, the results of this work indicate that the monocrystal data of Wachtman et al. [5] for alumina (α-Al_2O_3) and the biased monocrystal data of Kisi & Howard [10] for zirconia (t-ZrO_2) are the best data currently available. For dense polycrystalline α-Al_2O_3 the most reliable values calculated from monocrystal data are 402.7 GPa for the tensile modulus, 163.4 GPa for the shear modulus, 250.9 GPa for the bulk modulus and 0.23 for the Poisson ratio. In this case all calculated values are in reasonable agreement with measured values, taking into account the relatively large statistical errors of the latter. For dense polycrystalline t-ZrO_2 values calculated from monocrystal data are 201.1 GPa for the tensile modulus, 78.7 GPa for the shear modulus, 150.6 GPa for the bulk modulus and 0.28 for the Poisson ratio. In this case there is a discrepancy between calculated and measured values, especially for the bulk modulus, the measured values of which are approx. 180 ± 10 GPa and the Poisson ratio, the measured values of which are 0.31-0.32. This discrepancy for the bulk modulus and the Poisson ratio is indicative the fact that polycrystalline zirconia is less compressible than it would appear on the basis of monocrystal data alone, a fact that might be connected to the capability of zirconia to undergo to a certain extent plastic deformation. When approximate estimates for the effective elastic properties are required, we recommend the values E = 400 GPa and ν = 0.23 for alumina and E = 205 GPa and ν = 0.31 for zirconia (when the dopant is unspecified). When more detailed information is lacking, these approximate values, referring to dense and "pure" alumina and zirconia, respectively, can be used as benchmark values for fitting the dependence of effective elastic properties of porous alumina and zirconia (cf. Part 4) as well as for predicting the effective elastic properties of dense, statistically isotropic alumina-zirconia composite ceramics (cf. Part 5 of this series of papers).

Footnotes:

[1] The order of magnitude of this critical grain size is 0.5 μm and below, cf. e.g. [4].

[2] According to Howard & Kisi [11] the Reuss approximation works well for materials with a capacity for plastic deformation, such as metals and transformation-toughened ceramics.

[3] Quasi-isotropy does not necessarily require the individual grains to be isometric. But in the case of anisometric grains (e.g. tabular alumina or the non-equiaxed alumina grains possibly occurring due to excessive grain growth) these are not allowed to have a preferential orientation and their length has to be much smaller than the smallest dimension of the macroscopic body. That means, the results of this paper cannot be expected to apply to textured specimens, to alumina fibers or thin layers.

[4] When the Voigt and Reuss bounds are not too far apart, the difference between arithmetic average and other types of averages, e.g. the geometric or the harmonic average, is negligibly small.

[5] Interestingly, of the sets of values discussed above, all three violating the inversion relations are also violating Hill's theorem.

[6] Fortunately, a comparison of data for alumina listed in the NIST database [26,27] shows that e.g. the tensile modulus shows no significant differences when measured by a static method (e.g. three-point bending) or a dynamical method (e.g. resonant frequency or ultrasonic). From a physical viewpoint, this means that the difference between isothermal and adiabatic elastic moduli is small.

[7] A grain size dependence need not be taken into account, as long as the volume fraction of the interface regions (phase boundaries of small but finite thickness) are negligible. This is the case for typical submicron ceramics but might not be the case for nanomaterials, including nanocomposites.

[8] With respect to the relatively large statistical errors of measurement, these values should be sufficiently accurate. They should be used in cases where more detailed information concerning the individual samples in question is lacking.

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MAKROSKOPICKÉ ELASTICKÉ VLASTNOSTI KOMPOZITNÍ KERAMIKY NA BÁZI AL$_2$O$_3$ A ZRO$_2$ - ČÁST 3. VÝPOČET ELASTICKÝCH MODULŮ POLYKRYSTALICKÉHO AL$_2$O$_3$ A ZRO$_2$ NA ZÁKLADĚ DAT NAMĚŘENÝCH NA MONOKRYSTALECH

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V tomto článku je proveden výpočet makroskopických elastických modulů polykrystalického oxidu hlinitého (α-Al_2O_3, trigonální) a oxidu zirkoničitého (t-ZrO_2, tetragonální) ze složek tensoru elasticity, resp. inverzního tensoru elasticity (tj. ze složek matice tuhosti, resp. poddajnosti) určených pro monokrystaly α-Al_2O_3 a t-ZrO_2. Vypočtené hodnoty tzv. průměrů "VRH" (Voigt-Reuss-Hill) jsou porovnány s nejspolehlivějšími hodnotami naměřenými pro polykrystalický α-Al_2O_3 a t-ZrO_2 (databáze NIST z roku 2002). Pro hutný polykrystalický α-Al_2O_3 jsou nejspolehlivější hodnoty vypočtené z dat určených pro monokrystaly 402,7 GPa pro tahový modul (Youngův modul), 163,4 GPa pro smykový modul, 250,9 GPa pro objemový modul (modul stlačitelnosti) a 0,23 pro Poissonův poměr. V tomto případě jsou všechny vypočtené hodnoty v poměrně dobré shodě s naměřenými hodnotami (u kterých je třeba brát v úvahu relativně velké statistické chyby měření). Pro hutný polykrystalický t-ZrO_2 jsou hodnoty vypočtené z dat určených pro monokrystaly 201,1 GPa pro tahový modul, 78,7 GPa pro smykový modul, 150,6 GPa pro objemový modul a 0.28 pro Poissonův poměr. V tomto případě je mezi vypočtenými a naměřenými hodnotami patrný rozdíl, a to zejména u objemového modulu, jehož naměřené hodnoty jsou v oblasti cca. 180 ± 10 GPa, a u Poissonova poměru, jehož naměřené hodnoty jsou 0,31-0,32. Pro přibližný odhad makroskopických elastických vlastností hutných polykrystalických jednofázových materiálů doporučujeme pro α-Al_2O_3, resp. t-ZrO_2 použít následující hodnoty E = 400 GPa a ν = 0,23, resp. E = 205 GPa a ν = 0,31.