EFFECTIVE ELASTIC CONSTANTS OF PLAGIOCLASE FELDSPAR AGGREGATES IN DEPENDENCE OF THE ANORTHITE CONTENT – A CONCISE REVIEW

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Recent work on the elastic constants of plagioclase feldspars is reviewed. Based on the 21 elastic constants (stiffnesses) reported in the literature for triclinic plagioclase monocrystals of different composition, the effective elastic constants of dense, single-phase, polycrystalline plagioclase aggregates with isotropic microstructure are calculated via standard Voigt-Reuss-Hill averaging. Master curves show the good agreement of the constants obtained via the two approaches (experiment and simulation) and recall the fact that values reported in the older literature have been underestimated. Fit relations are given for the calculation of Young's modulus, shear modulus, bulk modulus, Poisson ratio and density in dependence of the composition. These fit relations may serve as handy tools for obtaining relevant input information for the calculation of effective elastic constants of multiphase ceramics produced with Ca and Na containing raw materials.

INTRODUCTION

Plagioclases, a series of tectosilicate minerals within the feldspar family with a composition between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$), are the most common rock-forming minerals in the Earth's crust [1]. Plagioclases occur as common phases in certain ceramics, especially in traditional ceramics prepared with calcium-containing raw materials. The majority of ceramic floor tiles (i.e. porcelain stoneware) are prepared by using natural felspathic sands as fluxing and tempering raw materials, and thus plagioclase crystals are one of the main constituents of the finished product [2]. Plagioclases can also crystallize if secondary raw materials (such as scrap glasses) are used [3, 4]. Traditional wall tiles (i.e. double-firing tiles) are often produced with calcite ($CaCO_3$) or wollastonite ($CaSiO_3$), which increases the strength of green tiles [5-9] due to its needle-like shape [10, 11] in a similar way as fiber reinforcements in composites. During firing, calcite and wollastonite react with other components, and calcium is available for the formation of anorthite or, if sodium is present, other plagioclases.

It is clear that in order to calculate the effective properties of multiphase materials the properties of each phase must be reliably known. In particular, the calculation of the elastic constants of statistically isotropic multiphase ceramics must be based on the elastic constants of the corresponding statistically isotropic dense polycrystalline single-phase materials. However, these constants for the polycrystalline materials are often not reliably known from experiments, either due to presence of residual porosity or due to the fact that pure polycrystalline materials are not always available. Therefore, reliable elastic constants for the individual phases can only be calculated from the elastic tensor components (stiffness matrix components) of the corresponding monocrystals.

Although to the best of our knowlegde the elastic constants of plagioclase feldspars have not been treated in the context of ceramics so far, fortunately a good deal of work has been done in geoscience, because of the importance of plagioclases as rock-forming minerals and the significance of the highly abundant plagioclase-containing rocks in the context of seismology [12, 13]. In particular, the elastic constants of plagioclase mono-crystals of different composition have been investigated both experimentally [14-18] and by simulation [19]. That means the complete information to calculate effective elastic constants of the corresponding dense

polycrystalline materials is in principle available. However, due to the traditional focus on seismological applications, all these papers provide averaged values only for the bulk and shear moduli and the sound velocities, not for the Young's modulus and Poisson ratio, which are the most important material properties from the viewpoint of applications in materials science, especially ceramics. Therefore in the present paper the most relevant recent results concerning elastic properties of plagioclase monocrystals are summarized (and compared to older data), Young's moduli and Poisson ratios are calculated as Voigt-Reuss-Hill averages and fitted master curves are given for the handy calculation of effective elastic constants of isotropic dense polycrystalline plagioclase materials in dependence of the anorthite content.

RESULTS AND DISCUSSION

From monocrystal data to effective elastic constants

Plagioclases are triclinic, therefore 21 independent elastic constants (stiffnesses) or elastic coefficients (compliances) are required to describe the elastic behavior of plagioclase monocrystals [20]. Until recently, the only data available for plagioclases of different composition (9, 53 and 58 mol. % of anorthite, denoted An09, An53 and An58, respectively) were 13 constants determined via ultrasonic velocity measurements for polysynthetically twinned (and thus pseudomonoclinic) crystal aggregates rather than true monocrystals [14-16].

These values, although frequently cited and used in seismology [12, 13], were based on an inadequate evaluation scheme (as shown in [17]), are prone to large uncertainties and have been estimated to be too low by approximately 10 %, probably mainly due to microcracks in the plagioclase samples used [21]. More recent experimental data have been obtained via impulsive stimulated light scattering (ISLS) [22] for albite [17] and plagioclases of different anorthite content (25, 37, 48, 60, 78 and 96 mol. %) [18]. Even more recently, *ab initio* calculations based on density functional theory (DFT) [23,24] have been performed for albite (An0), andesine/labradorite (An50) and anorthite (An100) [19], and generally good agreement with the aforementioned recent experimental data has been found.

Tables 1 and 2 list the room temperature elastic constants *E* (Young's modulus = tensile modulus), *G* (shear modulus), *K* (bulk modulus = compressive modulus) and *ν* (Poisson ratio) of dense single-phase, isotropic polycrystalline plagioclase aggregates, as calculated from the monocrystal elastic constants (stiffness and compliance matrix components based on [17-19]) via a standard Voigt-Reuss-Hill averaging procedure [25, 26]. The indices (subscripts) V, R and VRH that have been added to the symbols of the elastic moduli in these tables denote the Voigt bounds (calculated from the stiffnesses), Reuss bounds (calculated from the compliances) and Voigt-Reuss-Hill averages (i.e. the arithmetic means of the two aforementioned quantities), respectively. The symbol *Δ* has been used to denote the deviation of the VRH average from the extreme values (i.e. the Voigt and Reuss bounds). Poisson ratios have

Table 1. Adiabatic elastic constants *E* (Young's modulus) [GPa], *G* (shear modulus) [GPa], *K* (bulk modulus) [GPa] and *ν* (Poisson ratio) [dimensionless] of dense single-phase isotropic polycrystalline plagioclase aggregates and their end members albite (An0) and anorthite (An100), calculated from monocrystal elastic constants (based on the simulation results reported in [19]) via a standard Voigt-Reuss-Hill averaging procedure [25, 26]; for the shear and bulk moduli of An50 (LDA 1) a calculation error in [19] has been tacitly corrected here.

Plagioclase type	An0	An0	An0	An0	An50	An50	An50	An100
DFT approximation	LDA	GGA	LDA	LDA	LDA	LDA	LDA	LDA
Structural model	1	1	2	3	1	2	3	1
Density [g·cm^{-3}]	2.62	2.62	2.62	2.62	2.68	2.68	2.68	2.77
E_{VRH}	84.2	92.0	80.9	79.8	93.3	93.1	92.1	99.1
E_V	94.1	100.7	91.7	89.2	100.9	99.9	100.2	107.9
E_R	74.2	83.3	70.1	70.3	85.7	86.3	83.9	90.3
ΔE	10.0	8.7	10.8	9.5	7.6	6.8	8.1	8.8
G_{VRH}	33.8	36.0	32.3	32.4	36.5	36.5	35.9	38.3
G_V	38.1	39.7	37.0	36.7	39.8	39.5	39.5	41.9
G_R	29.6	32.3	27.5	28.2	33.2	33.6	32.4	34.6
ΔG	4.3	3.7	4.8	4.3	3.3	3.0	3.5	3.6
K_{VRH}	55.0	68.9	55.3	49.5	70.7	68.8	70.6	80.5
K_V	59.5	72.3	58.4	52.4	72.8	70.6	72.6	84.2
K_R	50.5	65.5	52.3	46.5	68.5	66.9	68.6	76.8
ΔK	4.5	3.4	3.1	3.0	2.4	1.8	2.0	3.7
ν	0.245	0.277	0.255	0.231	0.280	0.274	0.282	0.295

been calculated from the VRH averages of the elastic moduli via elasticity standard relations [20]. For the monocrystal data themselves the reader should refer to the original papers [17-19]. Both data sets concern adiabatic elastic constants, but the difference of adiabatic and isothermal elastic constants is negligibly small, viz. smaller than 1 % [17], similar as in the case of simple oxides [27].

The simulation results are based on either the local density approximation (LDA) [28] or the generalized gradient approximation (GGA) [29]. The former is used in connection with three different structural variants for albite (An0) and plagioclase An50, taking into account different degrees of disorder, more precisely the Al arrangements within the tetrahedral sites [19]. For albite,

model LDA 1 corresponds to ideally ordered albite (with Al occupying only specific types of tetrahedral sites), while models LDA 2 and LDA 3 correspond to albites with increasing disorder (with Al occupying partially all types of tetrahedral sites). For An50, models LDA 1 and LDA 2 correspond to an Al arrangement with lowest and higher energy, while model LDA 3 takes into account the effect caused by interchanging Na and Ca. The generalized gradient approximation (GGA) has been used only for ideally order albite.

Figures 1 through 4 show the elastic constants *E* (Young's modulus), *G* (shear modulus), *K* (bulk modulus) and *v* (Poisson ratio) of dense, single-phase, isotropic polycrystalline plagioclase aggregates in dependence of the anorthite content (in mol. %).
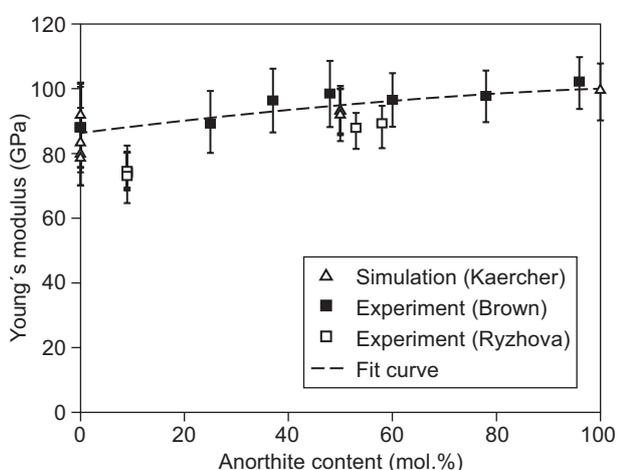

Figure 1. Effective Young's modulus of dense, single-phase, isotropic polycrystalline plagioclase aggregates in dependence of the anorthite content (in mol. %); simulation results by Kaercher et al. [19] (full triangles), experimental data by Brown et al. [17,18] (full squares) and Ryzhova [15] (empty squares) and fit curve based on [17-19].
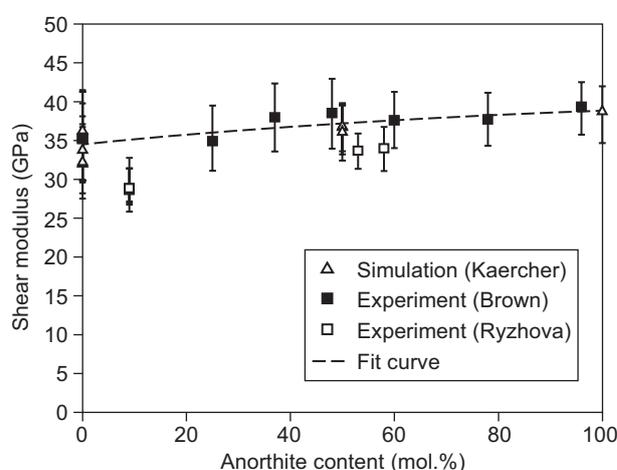

Figure 2. Effective shear modulus of dense, single-phase, isotropic polycrystalline plagioclase aggregates in dependence of the anorthite content (in mol. %); simulation results by Kaercher et al. [19] (full triangles), experimental data by Brown et al. [17, 18] (full squares) and Ryzhova [15] (empty squares) and fit curve based on [17-19].

Table 2. Adiabatic elastic constants *E* (Young's modulus) [GPa], *G* (shear modulus) [GPa], *K* (bulk modulus) [GPa] and *v* (Poisson ratio) [dimensionless] of dense single-phase isotropic polycrystalline plagioclase aggregates and their end members albite (An0) and anorthite (An100), calculated from monocrystal elastic constants (based on the experimental data reported in [17, 18]) via a standard Voigt-Reuss-Hill averaging procedure [25, 26].

| Plagioclase type	An0	An0	An25	An37	An48	An60	An78	An96
E_{VRH}	88.8	88.8	89.8	96.4	98.4	96.6	97.7	101.8
E_V	101.7	102.0	99.4	106.3	108.7	104.9	105.7	109.8
E_R	75.8	75.6	80.3	86.6	88.2	88.3	89.8	93.8
ΔE	13.0	13.2	9.6	9.9	10.2	8.3	8.0	8.0
G_{VRH}	35.5	35.6	35.2	37.9	38.4	37.6	37.7	39.1
G_V	41.2	41.4	39.4	42.3	42.9	41.2	41.1	42.4
G_R	29.8	29.8	31.1	33.5	33.9	34.0	34.3	35.7
ΔG	5.7	5.8	4.2	4.4	4.5	3.6	3.4	3.4
K_{VRH}	59.5	58.6	66.7	70.9	75.8	75.4	80.4	86.4
K_V	63.7	63.1	69.2	73.0	77.6	77.0	82.4	88.7
K_R	55.2	54.0	64.3	68.8	74.1	73.9	78.3	84.1
ΔK	4.3	4.5	2.4	2.1	1.8	1.6	2.0	2.3
v	0.250	0.247	0.275	0.273	0.283	0.286	0.297	0.303
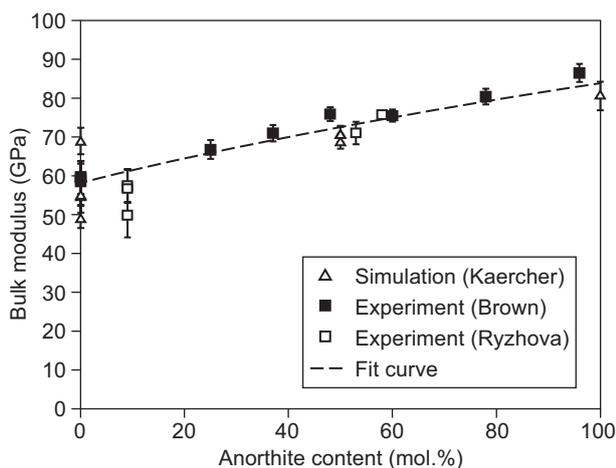
Figure 3. Effective bulk modulus of dense, single-phase, isotropic polycrystalline plagioclase aggregates in dependence of the anorthite content (in mol. %); simulation results by Kaercher et al. [19] (full triangles), experimental data by Brown et al. [17, 18] (full squares) and Ryzhova [15] (empty squares) and fit curve based on [17-19].
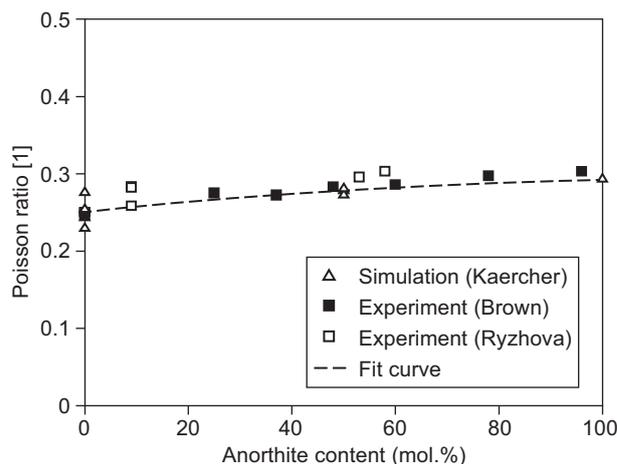

Figure 4. Effective Poisson ratio of dense, single-phase, isotropic polycrystalline plagioclase aggregates in dependence of the anorthite content (in mol. %); simulation results by Kaercher et al. [19] (full triangles), experimental data by Brown et al. [17, 18] (full squares) and Ryzhova [15] (empty squares) and fit curve based on [17-19].

Shown are the simulation results by Kaercher et al. [19] (full triangles), the recent experimental data by Brown et al. [17,18] (full squares) and, for the purpose of comparison, the old experimental data by Ryzhova [15] (empty squares).

It is evident that the simulation results (Kaercher) are in good agreement with the recent experimental data (Brown), while the old experimental data (Ryzhova) are significantly lower, especially for the Young's modulus and shear modulus, and slightly higher for the Poisson ratio. Therefore the latter have been discarded, and only the simulation results and recent experimental data have been fitted by second-order polynomials (non-linear regression using MS Excel®). Denoting the anorthite content (in mol. %) as C_{An}, the master curves obtained for the elastic constants (moduli in GPa and Poisson ratio dimensionless) are

$$E = 86.2 + 209.0 \times 10^{-3} \cdot C_{An} - 0.7 \times 10^{-3} \cdot C_{An}^{2},$$

$$G = 34.5 + 62.7 \times 10^{-3} \cdot C_{An} - 0.2 \times 10^{-3} \cdot C_{An}^{2},$$

$$K = 58.1 + 324.2 \times 10^{-3} \cdot C_{An} - 0.7 \times 10^{-3} \cdot C_{An}^{2},$$

$$\nu = 0.2511 + 0.7 \times 10^{-3} \cdot C_{An} - 0.003 \times 10^{-3} \cdot C_{An}^{2}.$$

These relations can be used to generate indispensible input information in future calculations of the effective elastic properties of multiphase ceramics, in particular silicate ceramics produced with Ca-containing raw materials where plagioclase is a typical constituent phase of the microstructure. Using these relations, the effective elastic constants of dense polycrystalline single-phase materials with isotropic microstructure can be calculated, as soon as the Ca-content of the plagioclase is known, e.g. from energy-dispersive spectrometry or electron-probe microanalysis. Subsequently these values, together with

the corresponding values for the other phases and the volume fractions of all phases, can be inserted e.g. into the Voigt and Reuss bounds for multiphase materials, also called Paul bounds [30, 31], in order to calculate the effective elastic constants of dense polycrystalline multiphase materials with isotropic microstructure.

In order to calculate the volume fractions from the mass fractions usually determined via quantitative X-ray diffraction phase analysis also the theoretical densities of all crystalline phases (and also the true density of the glass phase, if present) must be known. The theoretical density (in g·cm⁻³) of plagioclase is very well known [1, 19] and its dependence of the anorthite content (in mol. %), see Figure 5, can be expressed as

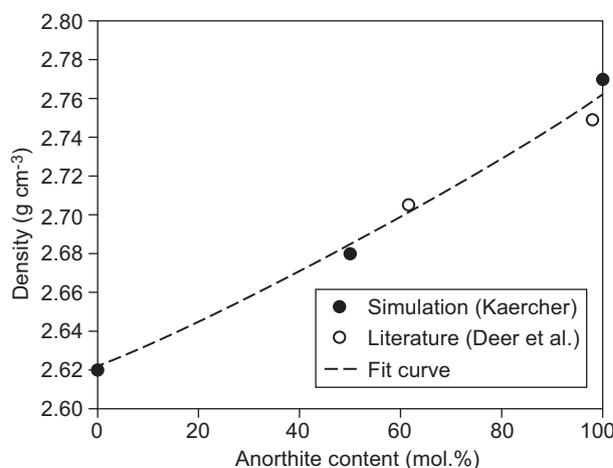$$\rho = 2.62 + 1.1 \times 10^{-3} \cdot C_{An} + 3.0 \times 10^{-6} \cdot C_{An}^{2}.$$

Figure 5. Theoretical density (in g·cm⁻³) of plagioclase as a function of the anorthite content (in mol. %); classical literature data based on experimental measurements (empty circles) [1] and recent simulation results (full circles) [19].

CONCLUSIONS AND SUMMARY

Recent work on the elastic constants of plagioclase feldspars has been reviewed. Based on the 21 elastic constants (stiffnesses) obtained experimentally by Brown et al. (using impulsive stimulated light scattering) and via computer simulation by Kaercher (using density functional theory) and reported in the literature for triclinic plagioclase monocrystals of different composition, the effective elastic constants of dense, single-phase, polycrystalline plagioclase aggregates with isotropic microstructure have been calculated via the standard Voigt-Reuss-Hill averaging procedure. Master curves obtained by fitting with second-order polynomials show the good agreement of the constants obtained via the two approaches (experiment and simulation) and recall the fact that values reported in the older literature (Ryzhova) have been underestimated. Fit relations are given for the calculation of Young's modulus, shear modulus, bulk modulus, Poisson ratio and density in dependence of the composition. These fit relations may serve as handy tools for obtaining relevant input information for the calculation of effective elastic constants of multiphase ceramics produced with Ca and Na containing raw materials.

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