

Correlations of the temperature and pressure dependencies of the elastic constants of zircon

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Abstract

The temperature dependencies of the single crystal elastic constants and the isotropic elastic moduli of zircon were reevaluated using the ultrasonic in-phase frequencies vs. temperature data and the thermal expansion coefficients. The bulk moduli of zircon at different temperatures were also calculated using the recently derived analytical expression by Garai and Laugier (J. Appl. Phys. 101, 023514 (2007)) utilizing the Anderson–Grüneisen parameter (δ) obtained from the pressure dependencies of the single crystal elastic constants. The temperature derivatives of the bulk modulus of zircon evaluated from the temperature derivatives of the single crystal elastic constants agree well with the corresponding values calculated from the analytical expressions utilizing the pressure derivative of the bulk modulus (δ). The results reveal good correlations between the ultrasonic measurements of the pressure and temperature derivatives of the single crystal elastic constants of zircon.

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1. Introduction

Zircon (ZrSiO_4) is one of the silicates that has relatively high density, high elastic stiffness and high melting temperature. It has the lowest compressibility and thermal expansion coefficients among the Si–O tetrahedral coordinated compounds except in its high-pressure scheelite-structure form. Zircon is effective to improve the mechanical properties, chemical stability and thermal shock resistance of ceramics. Zircon crystals occur in many rocks and bear importance for geological studies. Zircon crystals containing radioactive U and Th impurities convert into the metamict state over a long period of time with drastic reductions of the elastic moduli but without complete destruction of the structure. Zircon has been investigated as a host material for encapsulation and disposal of high-level nuclear fuels and radioactive wastes.

There are increased interests in the mechanical properties of the ceramic materials for advanced technological applications. The single crystal elastic constants are the fundamental param-

eters for the mechanical properties. They describe the response of crystals to the stress components and give information about the inter-atomic interactions and stability of materials.

In early pioneering studies the single crystal elastic constants of nonmetamict, synthetic and various metamict zircons were determined and their variations with temperature, pressure and natural nuclear irradiations were reported.^{1–5} These reports are quite unique because there are no other data in the literature about the pressure and temperature derivatives of the single crystal elastic constants of zircon. The isothermal bulk modulus (K_T) for the nonmetamict zircon obtained from the single crystal elastic constants is in good agreement with the corresponding data obtained from the high-pressure X-ray diffraction experiments and also from the theoretical computations.^{6–8} However, in a recent theoretical paper the bulk modulus, Debye temperature, thermal expansion coefficients and the specific heat of zircon were reported.⁹ The bulk modulus (K) of that report at room temperature is close to the value obtained from the elastic constants. But, the temperature derivatives of K_T and K_S (adiabatic) for zircon obtained from the slopes of the K vs. T graph of Ref. 9 above room temperature are about -0.015 and -0.007 $\text{GPa}/^\circ\text{C}$, respectively. These values are less than 75% of the value (-0.020 $\text{GPa}/^\circ\text{C}$)

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obtained from the temperature derivatives of the single crystal elastic constants.^{2,3} Such large differences in the $(dB/dT)_P$ values cannot be explained with the experimental uncertainties of the ultrasonic measurements.^{2,3}

During the ultrasonic measurements the lengths and density of the samples change as temperature changes. Such effects were taken into account for the calculations of the elastic wave velocities and elastic constants of zircon using the thermal expansion data available at the time.¹⁰ Since then additional, more detailed reports about the thermal expansion of zircon were published.^{11,12}

Recently, Garai and Laugier¹³ have derived an analytical solution for the temperature dependence of the bulk modulus from the fundamental thermodynamic equations. Their solution involves the volume thermal expansion coefficients, the bulk modulus and the Anderson–Grüneisen parameter (δ).¹⁴ The solution has been suggested to predict the bulk modulus and its temperature dependence.¹³ On the other hand, the temperature derivative of the bulk modulus $(dK/dT)_P$ can be expressed as the negative of the products $(\alpha_V K_T \delta)$, based on the definition of δ .¹⁴ The Anderson–Grüneisen parameter (δ)¹⁴ is equivalent to the pressure derivative of the bulk modulus $(dK/dP)_T$, and it is nearly constant at temperatures above about half of the Debye temperature.¹⁴ Therefore, the temperature derivatives of the bulk modulus $(dK/dT)_P$ at different temperatures can be calculated from the expression of Garai and Laugier¹³ and also from the product, $(-\alpha_V K_T \delta)$ by utilizing the δ value obtained from the pressure derivative of the bulk modulus and the thermal expansion coefficients. These statements correlate the pressure and temperature derivatives $(dK/dT)_P$, $(dK/dP)_T$ of a substance. To the present author's knowledge, such correlations of the experimental data of $(dK/dT)_P$ and $(dK/dP)_T$ obtained for the same or similar samples of a crystal has not been thoroughly examined to-date.

The ultrasonic data about the pressure and temperature derivatives of zircon,^{2,3,5} performed on the same or similar samples are quite suitable to test the correlations between the experimental $(dK/dT)_P$ and $(dK/dP)_T$ values. To achieve this purpose in this paper, the temperature derivatives of the single crystal elastic constants and the isotropic elastic moduli of zircon were recalculated using the measured ultrasonic normalized in-phase frequencies^{2,3} vs. temperature data and the detailed thermal expansion coefficients.^{11,12} Then, the temperature derivatives of the bulk modulus of zircon at different temperatures are calculated using the two expressions stated above,^{13,14} utilizing the δ value obtained from the pressure derivatives of the bulk modulus⁵ and the thermal expansion data.¹²

The temperature derivatives of the bulk modulus of zircon, obtained from the temperature derivatives of the single crystal elastic constants, agree well with the corresponding derivatives calculated from the analytical expressions by utilizing the δ value deduced from the pressure derivatives of the bulk modulus.⁵ Good correlations are found between the experimental values of $(dK/dT)_P$ and $(dK/dP)_T$ for zircon obtained from the ultrasonic measurements of the pressure and temperature derivatives of the single crystal elastic constants.

2. Computations, results and discussions

2.1. Temperature derivatives of the single crystal elastic constants of zircon

The temperature derivatives of the single crystal elastic constants of zircon were evaluated using the normalized in-phase frequencies and the thermal expansion coefficients.^{11,12} The elastic constants are proportional to the square of the normalized in-phase frequencies (F_R).^{2,3} The F_R values measured for the various ultrasonic wave modes in the zircon samples were observed to decrease linearly from room temperature (25 °C) up to 250 °C.^{2,3} The linear least square fits to the seven normalized in-phase frequencies associated with the various wave modes are reproduced below.^{2,3}

$$F_{R1} = 1.000 - 5.09 \times 10^{-5}(T - 25),$$

$$F_{R2} = 1.000 - 4.40 \times 10^{-5}(T - 25),$$

$$F_{R3} = 1.000 - 3.99 \times 10^{-5}(T - 25),$$

$$F_{R4} = 1.000 - 2.09 \times 10^{-5}(T - 25),$$

$$F_{R5} = 1.000 - 4.42 \times 10^{-5}(T - 25),$$

$$F_{R6} = 1.000 - 4.19 \times 10^{-5}(T - 25),$$

$$F_{R7} = 1.000 - 3.42 \times 10^{-5}(T - 25).$$

F_{R1} , F_{R2} , F_{R5} and F_{R6} are the normalized in-phase frequencies for the longitudinal wave (L) along [1 0 0], [0 0 1], [1 1 0] and [0 1 1], respectively. F_{R3} is the normalized in-phase frequency for the shear wave (S) along [0 0 1] polarized in [1 0 0]. F_{R4} is the normalized in-phase frequency for S along [1 0 0] polarized in [0 1 0] and F_{R7} is the normalized in-phase frequency for S along [0 1 1] polarized in [1 0 0].

The elastic constants at temperature T can be expressed in terms of the elastic constant at room temperature, 25 °C, the specimen length L and density ρ and the normalized in-phase frequency.^{2,3}

$$C(T) = C(25) \left[\frac{L(T)}{L(25)} \right]^2 \left(\frac{\rho(T)}{\rho(25)} \right) F_R^2$$

Based on this general equation the temperature dependencies of the elastic constants of zircon (tetragonal) can be expressed.^{2,3}

$$C_{11}(T) = C_{11}(25)(1 + \alpha_c(T - 25))^{-1} F_{R1}^2$$

$$C_{33}(T) = C_{33}(25)(1 + \alpha_a(T - 25))^{-2}(1 + \alpha_c(T - 25)) F_{R2}^2$$

$$C_{44}(T) = C_{44}(25)(1 + \alpha_a(T - 25))^{-2}(1 + \alpha_c(T - 25)) F_{R3}^2$$

$$C_{66}(T) = C_{66}(25)(1 + \alpha_c(T - 25))^{-1} F_{R4}^2$$

$$C_L(T) = C_L(25)(1 + \alpha_c(T - 25))^{-1} F_{R5}^2$$

Here α_a , and α_c are the linear thermal expansion coefficient along [1 0 0] and [0 0 1], respectively. C_L is the longitudinal moduli, ρv_L^2 , v_L being L propagated along [1 1 0] to obtain C_{12} . The expressions for the longitudinal moduli (C_Q) related to L along [0 1 1] and for the shear moduli (C_P) related to S along [0 1 1] polarized in [1 0 0] are given in Refs. 2,3. The former expression

Table 1
The temperature derivatives of the single crystal elastic constants of nonmetamict zircon

Elastic constant	dC/dT (GPa/°C), Refs. 2,3	dC/dT (GPa/°C), present
C_{11}	-0.0451	-0.0452
C_{33}	-0.0434	-0.0430
C_{44}	-0.0091	-0.0087
C_{66}	-0.0023	-0.0023
C_{12}	-0.0054	-0.0055
C_{13}	-0.0102	-0.0086
C_L		-0.0276
C_Q		-0.0349
C_P		-0.0057

The data in the second column are from Refs. 2,3, and in the last column are the reevaluated values.

utilizes F_{R6} and is used to calculate the temperature derivative of C_{13} . The later expression utilizes F_{R7} and is used to obtain cross check for the temperature derivatives of C_{44} and C_{66} .

In the original analysis^{2,3} the thermal expansion coefficients, α_a , α_c and α_V (the volume thermal expansion coefficient) of zircon reported by Bayer¹⁰ were used.^{2,3} In the present analysis more detailed thermal expansion data produced by a powder neutron diffraction study are used.¹¹ In that study¹¹ polynomial expressions of the lattice parameters as functions of temperature, $a(T)$, $c(T)$ between room temperature and 827 °C and also between 1127 and 1527 °C were reported. The parameters between room temperature and 827 °C are $a(T) = 6.6003 + 126 \times 10^{-7}T + 82 \times 10^{-10}T^2$ and $c(T) = 5.9783 + 29 \times 10^{-6}T + 67 \times 10^{-10}T^2$, here T is in K) used to evaluate the thermal expansion coefficients of zircon. The α_V values deduced from these polynomial expressions¹¹ are seen to be quite small near room temperature but they increase considerably at higher temperatures as compared with the corresponding values of the recently published theoretical thermal expansion data.⁹ Ref. 11, $\alpha_V = 10.82 \times 10^{-6}/^\circ\text{C}$ at 27 °C that increase 46% to $15.81 \times 10^{-6}/^\circ\text{C}$ at 727 °C. The corresponding data of Ref. 9 are quite different; $\alpha_V = 15 \times 10^{-6}/^\circ\text{C}$ at 27 °C that increase 13% to $17 \times 10^{-6}/^\circ\text{C}$ at 727 °C, obtained by converting the linear thermal expansion coefficients of Ref. 9 to the volume thermal expansion coefficients.

The elastic constants of the nonmetamict zircon at room temperature were reported in Refs. 1–5. The values of the elastic constants from room temperature up to 727 °C were calculated using the expressions listed above. The slopes of the C_{ij} - T graphs are labeled as the temperature derivatives of the related elastic constant. The temperature derivatives of C_{11} , C_{33} , C_{44} , and C_{66} are evaluated using the first 4 equations. The temperature derivatives of C_{12} , C_{13} and cross check for the temperature derivatives of C_{44} , and C_{66} are obtained by utilizing dC_L/dT , dC_Q/dT and dC_P/dT and F_{R5} , F_{R6} , F_{R7} , respectively. The temperature derivatives of the elastic constants in 25–250 °C are given in Table 1. The uncertainties of dC_{11}/dT , dC_{33}/dT and dC_{44}/dT are about 2–3%; the uncertainty of dC_{66}/dT is about 5% due to its relatively small magnitude. The uncertainties of dC_{12}/dT , and especially of dC_{13}/dT could be higher as the other elastic constants take part in their calculations. Special care was paid for the calculations of C_{13} to reduce the uncertainty in dC_{13}/dT .

It is noted that the elastic constants decrease linearly up to 250 °C. The similar linear decreases are expected for higher temperatures up to 827 °C. The calculated temperature derivatives of the elastic constants of zircon are almost same as those reported earlier.^{2,3} The lengths and density factors do not have significant affects; the major changes in the derivatives arise from the temperature dependencies of the normalized in-phase frequencies. There are no other data in the literature about the temperature derivatives of the single crystal elastic constants of zircon with which to compare the present values.

2.2. Temperature derivatives of the isotropic elastic moduli of zircon

2.2.1. dK/dT and dG/dT obtained from the temperature derivatives of the elastic constants (experimental)

The bulk and shear moduli (K , G) of zircon at different temperatures were calculated using the Voigt, Reuss and Hill approaches.¹⁵ For the tetragonal system K and G are expressed as follows.

$$K_V = \frac{(2C_{11} + C_{33})}{9} + \frac{2(C_{12} + 2C_{13})}{9} \quad (1)$$

$$G_V = \frac{(2C_{11} + C_{33})}{15} - \frac{(C_{12} + 2C_{13})}{15} + \frac{(2C_{44} + C_{66})}{5} \quad (2)$$

$$\frac{1}{K_R} = 2S_{11} + S_{33} + 2(S_{12} + 2S_{13}) \quad (3)$$

$$\frac{1}{G_R} = \frac{4(2S_{11} + S_{33}) - 4(S_{12} + 2S_{13}) + 3(2S_{44} + S_{66})}{15} \quad (4)$$

Here, the subscripts V and R denote Voigt and Reuss values, respectively, and S_{ij} are the elastic compliance constants evaluated from the elastic stiffness constants, C_{ij} .

The K and G values of zircon are calculated from room temperature up to 827 °C with the Hill approach (the mean of the Voigt and Reuss values). The room temperature values of K and G are given in Table 2 and the calculated K values were plotted vs. temperature in Fig. 1. The $(dK/dT)_P$ and $(dG/dT)_P$ of zircon obtained from the temperature derivatives of the elastic constants in 25–250 °C range are: $(dK/dT)_P = -0.0202 \text{ GPa}/^\circ\text{C}$ and $(dG/dT)_P = -0.0094 \text{ GPa}/^\circ\text{C}$. The magnitudes of the $(dK/dT)_P$ values slightly decrease as temperature increases toward 800 °C. The K_V and K_R values are close to each other, but the large difference in the G_V and G_R values indicate a high degree of shear anisotropy of the zircon structure. The relatively small magnitudes of C_{66} and its pressure and temperature derivatives are related to the layer-like arrangements of atoms along the c -axis in the structure of zircon as discussed before.^{2–5} There are no

Table 2
The room temperature values of the isotropic bulk and shear moduli of zircon (in GPa) calculated from the single crystal elastic constants by the Voigt, Reuss and Hill approaches

Method moduli	Voigt, upper bounds	Reuss, lower bounds	Hill, averages
K (GPa)	229.5	224.4	226.9
G (GPa)	120.0	98.4	109.2

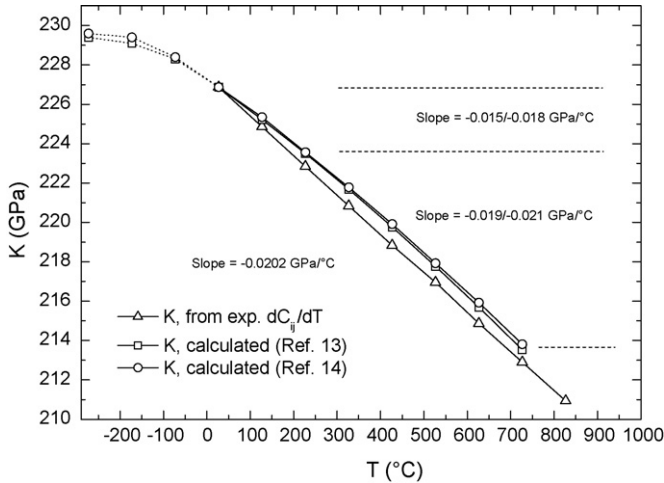


Fig. 1. The bulk moduli vs. temperature plots for zircon, deduced from the temperature derivatives of the single crystal elastic constants, calculated using Eqs. (5) and (6) (from Refs. 13,14). The slopes of the three curves are about the same in 350–550 °C range.

other experimental data in the literature with which to compare the temperature derivatives of K and G of zircon.

2.2.2. dK/dT obtained from the analytical expressions utilizing the Anderson–Grüneisen parameter and the thermal expansion coefficients (theoretical)

The Anderson–Grüneisen parameter (δ) is defined as,

$$\delta = - \left(\frac{1}{\alpha_V K} \right) \times \left(\frac{dK}{dT} \right)_P \quad (5)$$

Eq. (5) can be written in the following form as recently stated by Garai and Laugier.¹³

$$K_T = K_{T_0} e^{-\int_{T_0}^T \alpha_V(T) \delta(T) dT} \quad (6)$$

Here K_T is the bulk modulus at temperature T and K_{T_0} is the bulk modulus at the reference temperature T_0 . The

Anderson–Grüneisen parameter (δ) is equivalent to the pressure derivative of the bulk modulus $(dK/dP)_T$ as shown by Anderson.¹⁴ The pressure derivative of the bulk modulus of zircon was determined^{3,5,7} to be 6.5. The $(dK/dT)_P$ values for zircon are calculated numerically using Eqs. (5) and (6) successively from room temperature up to 837 °C with small temperature intervals using the initial $K=227$ GPa, $\delta=(dK/dP)_T=6.5$, and the average $\alpha_V(T)$ values for the intervals deduced from the thermal expansion data of Ref. 11. The calculated bulk modulus vs. temperature data for 100 °C intervals are listed in Table 3 and plotted in Fig. 1. The K – T plots and the $(dK/dT)_P$ values of zircon calculated using Eqs. (5) and (6) are about the same since the equations are equivalent to each other. The $(dK/dT)_P$ values vary from about $-0.015/-0.018$ GPa/°C (between 27 and 127 °C) and from about $-0.019/-0.021$ GPa/°C (between 227 and 727 °C). These data for the temperature range from about 300 °C up to the Deye temperature¹⁶ are in good agreement with the experimental $(dK/dT)_P$ values (about -0.020 GPa/°C) reported above.

Small deviations of the calculated slopes (using the Eqs. (5) and (6)) from the experimental value (-0.020 GPa/°C) at room and high temperatures are noticeable. It is noted that the experimental α_V values of zircon used here are rather small near room temperature¹¹ but they increase at higher rates as compared with the recently published theoretical thermal expansion data.⁹

The calculated values of K and the slopes $(dK/dT)_P$ at different temperatures sensitively depend on the value of the Anderson–Grüneisen parameter in addition to the thermal expansion coefficients. The $(dK/dP)_T$, (K') value used here (6.5) was determined from the ultrasonic measurements of the pressure derivatives of the elastic constants.^{2,3,5} The accuracy of the ultrasonic measurements was discussed in Ref. 5. Several authors¹⁷ have assigned K' as 4.0 (or 6.5) for fitting compression data for zircon to the equations of state. Recently, Marques et al.⁷ have carried out experimental and theoretical studies about the structure and stability of zircon under hydrostatic pressure. Compared and discussed in detail were the contradicting data

Table 3
The bulk moduli of zircon at different temperatures: (a) determined from the temperature derivatives of the single crystal elastic constants, (b, c) calculated from the expression of Garai and Laugier, Eq. (6), and the defining expression of the Anderson–Grüneisen parameter, Eq. (5), respectively

T (°C)	$\alpha_V (\times 10^{-6}/^\circ\text{C})$	K (GPa) (a) present, from exp. dC_{ij}/dT	K (GPa) (b) calculated Eq. (6)	$(dK/dT)_P$ (b) GPa/°C Eq. (6)	K (GPa) (c) calculated Eq. (5)	$(dK/dT)_P$ (c) GPa/°C Eq. (5)
–273			229.4	0	229.6	0
–173	3.2		229.1	–0.012	229.4	–0.012
–73	8.1		228.3	–0.014	228.4	–0.014
27	10.820	226.87	226.87	–0.0164	226.87	–0.0152
127	11.534	224.85	225.23	–0.0173	225.35	–0.0178
227	12.250	222.84	223.50	–0.0182	223.57	–0.0178
327	12.964	220.84	221.68	–0.0191	221.79	–0.0187
427	13.677	218.84	219.77	–0.0200	219.92	–0.0199
527	14.389	216.96	217.77	–0.0208	217.93	–0.0201
627	15.100	214.87	215.69	–0.0216	215.92	–0.0211
727	15.810	212.90	213.53			
827	16.519	210.94				

The K and $(dK/dT)_P$ data obtained by using Eqs. (5) and (6) are about the same since the equations are equivalent to each other. The volume thermal expansion coefficients are also listed.¹¹ The calculations of K and $(dK/dT)_P$ values are extended below room temperature by utilizing the low temperature thermal expansion data.¹²

for K and K' in the literature for zircon and classified them in two sets, as set I, K : 225–230 GPa, K' : 6.5 (experimentally determined value) and set II, K : 199–205 GPa, K' : 4 ('plausible fixed value'). In this most recent study about the subject the experimental values for K and K' were reported as 225 ± 8 GPa and 6.5 ± 1.6 , respectively, supporting the data in set I and the present author's early ultrasonic data for K and K' .

It is noted that the above analyses are valid for the non-metamict zircon crystals. The bulk moduli and their pressure and temperature derivatives as well as the thermal expansion coefficients of the zircon samples may drastically change depending on their metamict (radiation damaged) conditions.^{3,4} The presence of major impurities in the samples may also affect the bulk moduli and their pressure and temperature derivatives.

3. Conclusions

The temperature derivatives of the single crystal elastic constants of zircon were reevaluated. The temperature derivatives of the bulk modulus of zircon determined from the temperature derivatives of the single crystal elastic constants agree well with the values calculated using the theoretical expressions of Anderson,¹⁴ Garai and Laugier,¹³ especially for temperatures close to the Debye temperature. It is noted that in the expressions, δ obtained from the pressure derivatives of the single crystal elastic constants of zircon were used. The analyses presented above show good correlations between the pressure and temperature derivatives of the bulk modulus of zircon derived from the pressure and temperature derivatives of the single crystal elastic constants.^{1–5} This is highly interesting considering the degree of structural and thermo elastic anisotropy possessed by such a highly incompressible crystal as zircon.

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References

- Ozkan, H., Cartz, L. and Jamieson, J. C., Elastic constants of nonmetamict zirconium silicate. *J. Appl. Phys.*, 1974, **45**(2), 556–562.
- Ozkan, H., Cartz, L. and Fisher, E. S., Temperature dependence of the elastic constants of zircon. *Rev. Int. Htes. Temp. Refract.*, 1975, **12**(1), 52–57.
- Ozkan, H., Elastic properties of zircons, a study of pressure, temperature and irradiation effects on the elastic moduli of zircon. *Ph.D. Thesis*, 1975, Marquette University, Milwaukee, WI, USA.
- Ozkan, H., Effect of nuclear radiation on the elastic moduli of zircon. *J. Appl. Phys.*, 1976, **47**(11), 4772–4779.
- Ozkan, H. and Jamieson, J. C., Pressure dependence of the elastic constants of nonmetamict zircon. *Phys. Chem. Mine.*, 1978, **2**, 215–224.
- Hazen, R. M. and Finger, L. W., Crystal structure and compressibility of zircon at high pressure. *Am. Mineral.*, 1979, **64**, 196–201.
- Marques, M., Florez, M., Recio, J. M., Gerward, L. and Olsen, J. S., Structure and stability of $ZrSiO_4$ under hydrostatic pressure. *Phys. Rev. B*, 2006, **74**, 014104.
- Yao, H., Ouyang, L. and Ching, W. Y., Ab initio calculation of elastic constants of ceramic crystals. *J. Am. Ceram. Soc.*, 2007, **90**, 3194–3204.
- Terki, R., Bertrand, H. and Aourang, H., Full potential investigations of structural and electronic properties of $ZrSiO_4$. *Microelectr. Eng.*, 2005, **81**, 514–523.
- Bayer, G., Thermal expansion of ABO_4 compounds with zircon- and scheelite structures. *J. Less Common Met.*, 1972, **26**, 255–262.
- Mursic, Z., Vogt, T. and Fray, F., High temperature neutron powder diffraction study of $ZrSiO_4$ up to 1900 K. *Acta Cryst.*, 1992, **B48**, 584–590.
- Chaplot, S. L., Mittal, R., Busetto, E. and Lausi, A., Thermal expansion in zircon and almandine: synchrotron X-ray diffraction and lattice dynamical study. *Phys. Rev. B*, 2002, **66**, 064302.
- Garai, J. and Laugier, A., The temperature dependence of the isothermal bulk modulus at 1 bar pressure. *J. Appl. Phys.*, 2007, **101**, 023514.
- Anderson, O. L., *Equation of State of Solids for Geophysics and Ceramic Science*. Oxford University Press, Oxford, 1995, Pages, 16, 21–23.
- Hill, R., The elastic behavior of a crystalline aggregate. *Proc. Phys. Soc. Lond.*, 1952, **A65**, 349–354.
- Ozkan, H. and Cartz, L., Anisotropic thermo physical properties of zircons. In *AIP Conference Proceedings, No 17, Thermal Expansion 1973*, 21–33, ed. R. E. Taylor and G. L. Denman. AIP, New York, 1974.
- Westrenen, W., Frank, M. R., Hanchar, J. M., Fei, Y., Finch, R. J. and Zha, C.-S., In situ determination of the compressibility of synthetic pure zircon ($ZrSiO_4$) and the onset of the zircon-reidite phase transition. *Am. Mineral.*, 2004, **89**, 197–203.