

Temperature-Dependent Bulk Modulus Model for Solid Single Crystals

Jiaying Shao, Weiguo Li,* Yong Tao, Jianzuo Ma, Ziwei Cao, Haibo Kou, Yong Deng, Liming Chen, and Zhaoliang Qu

In this study, a temperature-dependent bulk modulus model without any adjustable parameters for solids single crystals is developed based on an equivalent relation between deformation energy and heat energy. This model uncovers the quantitative relation between the temperature-dependent bulk modulus, heat capacity, boiling point, enthalpy of solid-state phase transition, enthalpy of fusion, enthalpy of vaporization, and volume coefficient of thermal expansion. As examples, the temperature-dependent adiabatic bulk moduli of α -Al₂O₃, MgO, Si, Ti, SrF₂, CaF₂, and MgF₂ are predicted, and are in good agreement with the available experimental results. This study provides a new and practical method to quantitatively characterize the temperature-dependent bulk modulus of solid single crystals.


1. Introduction

Solid single crystals as the temperature-resistant structural components have been widely applied in the high temperature fields such as aerospace, nuclear energy, and military applications due to their excellent optic properties, mechanical properties, and chemical stability. For example, sapphire (α -Al₂O₃) can be used as the high-temperature optic window materials in the space shuttles or missiles. Bulk modulus is an important evaluation index of the high temperature applications of solid single crystals. Knowledge of their temperature-dependent bulk modulus helps to characterize their compressibility, cohesive properties, relative stability and transformations of phases, and formation of lattice defects especially at elevated temperatures.^[1]

Dr. J. Shao, Prof. W. Li, Dr. Y. Tao, Dr. J. Ma, Z. Cao, Dr. H. Kou, Dr. Y. Deng, Prof. L. Chen
College of Aerospace Engineering
Chongqing University
Chongqing 400030, China
E-mail: wgli@cqu.edu.cn

Dr. J. Shao, Prof. W. Li
State Key Laboratory of Coal Mine Disaster Dynamics and Control
Chongqing University
Chongqing 400030, China

Dr. Z. Qu
Institute of Advanced Structure Technology
Beijing Institute of Technology
Beijing 100081, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssb.201800286>.

DOI: 10.1002/pssb.201800286

Experimentally, ultrasonic measurements and resonance techniques are often used to determine the bulk moduli of solid single crystals at different temperatures. Ultrasonic measurements are limited to about 800 K due to the problems caused by the temperature behavior of transducers and glues; resonance techniques does not need to glue the specimen, and can be applicable at temperatures above 800 K.^[2] Using these methods, numerous experimental studies^[2–3] have been conducted, and indicate that bulk modulus of solid single crystals has a significant temperature dependence. In order to characterize the temperature dependence, many important theoretical models^[1b,2,4] have been

developed. However, it can be observed that in these models^[1b,2,4a–e] there is a necessary adjustable parameter, Anderson–Grüneisen parameter, which needs to be determined from the fitting function of sufficient bulk modulus data measured at certain high temperatures. Aguado et al.^[4f] established a successful phenomenological model relating the temperature-dependent bulk modulus to the spectroscopic properties of binary cubic crystals. In summary, although numerous empirical characterization methods were provided, the quantitative inherent relation between the temperature-dependent bulk modulus of solid single crystals and their basic material parameters remains unknown.

In this study, a temperature-dependent bulk modulus model without any adjustable parameters is developed for solids single crystals. The model is verified by comparison with the available experimental results of seven types of solid single crystals. The quantitative relation between the temperature-dependent bulk modulus of solid single crystals and heat capacity (or relative enthalpy), boiling point, enthalpy of solid-state phase transition, enthalpy of fusion, enthalpy of vaporization, and volume coefficient of thermal expansion is found. This study deals with the quantitative characterization on the temperature-dependent bulk modulus of solids single crystals.

2. Theory

In this section, the temperature-dependent bulk modulus model for solid single crystals was deduced. From the viewpoint of energy, Li et al.^[5] proposed a modeling idea for temperature-dependent properties of materials, which has been successfully applied to characterize various temperature-dependent properties, such as

fracture strength^[5–6] and yield strength.^[7] Based on this modeling idea, for a particular solid we assume that, when it undergoes a small uniform volumetric strain ε_0 under external compressive loading at different temperatures, there exists a constant total energy U_{total} which is composed of deformation energy $U_D(T)$ and heat energy $U_H(T)$. Due to their different influence mechanisms on the material deformation, the two energy should have a quantitative equivalent relation.^[5] The total energy U_{total} is expressed as:

$$U_{\text{total}} = U_D(T) + kU_H(T) \quad (1)$$

where k is the dimensionless ratio coefficient between the deformation energy and the heat energy. As the effects of deformation energy and heat energy on the material deformation are not completely equivalent, k is used to reflect their transformational relation, which is an assumed constant.^[5–7] This coefficient does not need to be determined, and will be eliminated in the following modeling process.

When the material undergoes a small uniform volumetric strain ε_0 at different temperatures T under compressive loading, assuming its deformation obeys the linear-elastic relation, the deformation energy density $U_d(T)$ of material could be given as^[8]:

$$U_d(T) = \frac{1}{2} B(T) \varepsilon_0^2 \quad (2)$$

where $B(T)$ is the bulk modulus at temperature T .

Then, the deformation energy in the material after deformation is given as:

$$U_D(T) = \int U_d(T) dV = \frac{1}{2} B(T) \varepsilon_0^2 V(T) \quad (3)$$

where $V(T)$ represents the volume of material at temperature T .

The heat energy $U_H(T)$, used to heat the material from 0 to T (in Kelvin), can be obtained:

$$U_H(T) = m \left(\int_0^T C_p(T) dT + \Delta H_t + \Delta H_m + \Delta H_b \right) \quad (4)$$

where m is the mass of material; $C_p(T)$ is the specific heat capacity at constant pressure p ; according to the definition of the heat energy $U_H(T)$, there exists:

$$\begin{cases} \Delta H_t = 0, \Delta H_m = 0, \Delta H_b = 0; T < T_{st} \\ \Delta H_t = \Delta H_T, \Delta H_m = 0, \Delta H_b = 0; T_{st} \leq T < T_M \\ \Delta H_t = \Delta H_T, \Delta H_m = \Delta H_M, \Delta H_b = 0; T_M \leq T < T_B \\ \Delta H_t = \Delta H_T, \Delta H_m = \Delta H_M, \Delta H_b = \Delta H_B; T = T_B \end{cases} \quad (5)$$

where T_{st} is the temperature when the solid-state phase transition occurs; T_M is the melting point; T_B is the boiling point; ΔH_T , ΔH_M , and ΔH_B are enthalpy of solid-state phase transition, enthalpy of fusion and vaporization, respectively.

Then, substituting Equations (3) and (4) into Equation (1), the constant total energy U_{total} can be expressed as:

$$U_{\text{total}} = \frac{1}{2} B(T) \varepsilon_0^2 V(T) + km \left(\int_0^T C_p(T) dT + \Delta H_t + \Delta H_m + \Delta H_b \right) \quad (6)$$

When $T = T_0$ (T_0 is the reference temperature and can be set as an arbitrary temperature; it is set as room temperature (generally lower than T_{st}) considering that the room temperature data can be conveniently obtained), from Equations (6) and (5) one can obtain:

$$U_{\text{total}} = \frac{1}{2} B(T_0) \varepsilon_0^2 V(T_0) + km \left(\int_0^{T_0} C_p(T) dT \right) \quad (7)$$

When $T = T_B$, the material will entirely convert into gas after continuously heated; for ideal gas, $B(T_B) = \gamma(T_B) p = \frac{C_p(T_B)}{C_v(T_B)} p$ under the adiabatic condition or $B(T_B) = p$ under the isothermal condition, where p is the pressure, 1 atm ($C_v(T_B)$ is the specific heat capacity at constant volume); $B(T_B)$ is quite small, comparing with the bulk modulus of material in the solid or liquid state, in GPa. Thus, when $T = T_B$, the small deformation energy term is ignored; similarly, from Equations (6) and (5) we can obtain:

$$U_{\text{total}} = km \left(\int_0^{T_B} C_p(T) dT + \Delta H_t + \Delta H_m + \Delta H_b \right) \quad (8)$$

Combining Equation (6) with Equation (7), we can obtain:

$$\begin{aligned} & \frac{1}{2} \varepsilon_0^2 [B(T_0) V(T_0) - B(T) V(T)] \\ & = km \left(\int_{T_0}^T C_p(T) dT + \Delta H_t + \Delta H_m + \Delta H_b \right) \end{aligned} \quad (9)$$

Combining Equation (7) with Equation (8), yields:

$$k = \frac{1}{2} B(T_0) \varepsilon_0^2 V(T_0) \left/ m \left(\int_{T_0}^{T_B} C_p(T) dT + \Delta H_t + \Delta H_m + \Delta H_b \right) \right. \quad (10)$$

Moreover, the temperature-dependent volume of material can be estimated as:

$$V(T) = V(T_0) \exp \left(\int_{T_0}^T \alpha_v(T) dT \right) \quad (11)$$

where $\alpha_v(T)$ is the volume coefficient of thermal expansion at temperature T .

Then, substituting Equations (10) and (11) into Equation (9), the temperature-dependent bulk modulus model for solid single crystals is obtained:

Table 1. The material parameters used in the model calculations for the seven types of solid single crystals.^[2,3,9–19]

	$\alpha\text{-Al}_2\text{O}_3$	MgO	Si	Ti	SrF ₂	CaF ₂	MgF ₂
$B(T_0)$, GPa	253.8 ^[2]	163.9 ^[2]	91.9 ^[3a]	107.4 ^[3b]	71.3 ^[3c]	84.5 ^[3c]	101.9 ^[3d]
T_M , K	2327 ^[9]	3098 ^[9]	1685 ^[9]	1933 ^[9]	1673 ^[9]	1691 ^[9]	1536 ^[9]
T_B , K	3253.2 ^[10]	3533 ^[9]	3492 ^[9]	3575 ^[9]	2733 ^[11]	2783 ^[9]	2605 ^[9]
ΔH_T , J g ^{−1}	0	0	0	86.5 ^[9]	0.636 ^[12]	61.1 ^[9]	0
ΔH_M , J g ^{−1}	1161.3 ^[9]	1920.7 ^[9]	1800 ^[9]	389 ^[9]	143.2 ^[9]	380.5 ^[9]	933.5 ^[9]
ΔH_B , J g ^{−1}	19380 ^[11]	8206 ^[13]	10610 ^[11]	8907 ^[9]	2547.4 ^[12]	3956.5 ^[12]	4385.5 ^[9]
$\alpha_V(T)$, K ^{−1}	$10^{-5} \times (2.226 + 5.899 \times 10^{-4} \times T - 7.138 \times 10^4 \times T^{-2})$, $\alpha\text{-Al}_2\text{O}_3$ ^[14] ; $10^{-5} \times (3.781 + 7.625 \times 10^{-4} \times T - 8.064 \times 10^4 \times T^{-2})$, MgO ^[14] ; $3 \times \{3.725 \times (1 - \exp[-5.88 \times 10^{-3} \times (T - 124)]) + 5.548 \times 10^{-4} \times T\} \times 10^{-6}$, Si ^[15] ; $2.507 \times 10^{-5} + 1.021 \times 10^{-8} \times T - 0.177 \times T^{-2}$, Ti ^[16] ; $3 \times (1.416 \times 10^{-5} + 1.555 \times 10^{-8} \times T)$, SrF ₂ ^[17] ; $3 \times \{1.885 \times 10^{-5} + 1.67 \times 10^{-8} \times (T - 273.15) + 5.5 \times 10^{-12} \times (T - 273.15)^2\}$, CaF ₂ ^[18] ; $1.14 \times 10^{-5} + 1.05 \times 10^{-8} \times T$, MgF ₂ ^[19]						
$C_p(T)$, J g ^{−1} K ^{−1}	$\left\{ \begin{array}{l} (103.851 + 26.267 \times 10^{-3} \times T - 29.091 \times 10^5 \times T^{-2})/101.96; 298\text{K} \leq T \leq 800\text{K} \\ (120.516 + 9.192 \times 10^{-3} \times T - 48.367 \times 10^5 \times T^{-2})/101.96; 800\text{K} \leq T \leq 2327\text{K}, \alpha\text{-Al}_2\text{O}_3^{[9]} \\ 1.421; 2327\text{K} \leq T \leq 3253.15\text{K}; \end{array} \right.$ $\left\{ \begin{array}{l} (48.953 + 3.138 \times 10^{-3} \times T - 11.422 \times 10^5 \times T^{-2})/40.3; 298\text{K} \leq T \leq 3098\text{K} \\ 1.505; 3098\text{K} \leq T \leq 3533\text{K}, \text{MgO}^{[9]} \end{array} \right.$; $\left\{ \begin{array}{l} (22.803 + 3.849 \times 10^{-3} \times T - 3.515 \times 10^5 \times T^{-2})/28.08; 298\text{K} \leq T \leq 1685\text{K} \\ 0.969; 1685\text{K} \leq T \leq 3492\text{K}, \text{Si}^{[9]} \end{array} \right.$; $\left\{ \begin{array}{l} (22.133 + 10.251 \times 10^{-3} \times T)/47.867; 298\text{K} \leq T \leq 1155\text{K} \\ (19.832 + 7.908 \times 10^{-3} \times T)/47.867; 1155\text{K} \leq T \leq 1933\text{K}, \text{Ti}^{[9]}; \\ 0.743; 1933\text{K} \leq T \leq 3575\text{K} \end{array} \right.$ $\left\{ \begin{array}{l} (75.019 + 9.54 \times 10^{-3} \times T)/125.62; 298\text{K} \leq T \leq 1673\text{K} \\ 0.799; 1673\text{K} \leq T \leq 2733\text{K}, \text{SrF}_2^{[9]}; \end{array} \right.$ $\left\{ \begin{array}{l} (59.831 + 30.46 \times 10^{-3} \times T + 1.966 \times 10^5 \times T^{-2})/78.075; 298\text{K} \leq T \leq 1424\text{K} \\ (107.989 + 10.46 \times 10^{-3} \times T)/78.075; 1424\text{K} \leq T \leq 1691\text{K}, \text{CaF}_2^{[9]}; \\ 1.281; 1691\text{K} \leq T \leq 2783\text{K} \end{array} \right.$ $\left\{ \begin{array}{l} (70.835 + 10.544 \times 10^{-3} \times T - 9.205 \times 10^5 \times T^{-2})/62.3; 298\text{K} \leq T \leq 1536\text{K} \\ 1.5158; 1536\text{K} \leq T \leq 2605\text{K}, \text{MgF}_2^{[9]} \end{array} \right.$						

$$B(T) = \frac{B(T_0)}{\exp\left(\int_{T_0}^T \alpha_V(T) dT\right)} \left\{ 1 - \frac{\left(\int_{T_0}^T C_p(T) dT + \Delta H_T + \Delta H_M + \Delta H_B\right)}{\left(\int_{T_0}^T C_p(T) dT + \Delta H_T + \Delta H_M + \Delta H_B\right)} \right\} \quad (12)$$

Equation (12) relates the bulk modulus at different temperatures to that at a reference temperature, heat capacity (or relative enthalpy), boiling point, enthalpy of solid-state phase transition, enthalpy of fusion, enthalpy of vaporization, and volume coefficient of thermal expansion.

3. Results and Discussion

The temperature-dependent adiabatic bulk moduli of $\alpha\text{-Al}_2\text{O}_3$, MgO, Si, Ti, SrF₂, CaF₂, and MgF₂ are calculated using

Equation (12), and compared with the available reported experimental results. Reference temperature T_0 is all set as room temperature. The material parameters used in the model calculations for these solid single crystals are given in **Table 1**.^[2,3,9–19] In **Figure 1a**, our model predictions are very close to the experimentally-measured adiabatic bulk modulus of $\alpha\text{-Al}_2\text{O}_3$.^[2] Sivasubramanian's model shows reasonable agreement with the adiabatic bulk moduli of $\alpha\text{-Al}_2\text{O}_3$ below 650 K.^[4a] The predicted results by Shang et al.^[20] using first-principles calculations show good agreement with the adiabatic bulk moduli of $\alpha\text{-Al}_2\text{O}_3$ between 800 and 1800 K. In **Figure 1b** and **c**, the predicted results by Equation (12) also agrees well with the experimental values of MgO,^[2] Si^[3a] (below 1000 K), and Ti^[3b] (below 750 K). The first principles quasiharmonic calculation results by Wu et al. and Wentzcovitch et al.^[21] are close to the experimental values of MgO between room temperature and

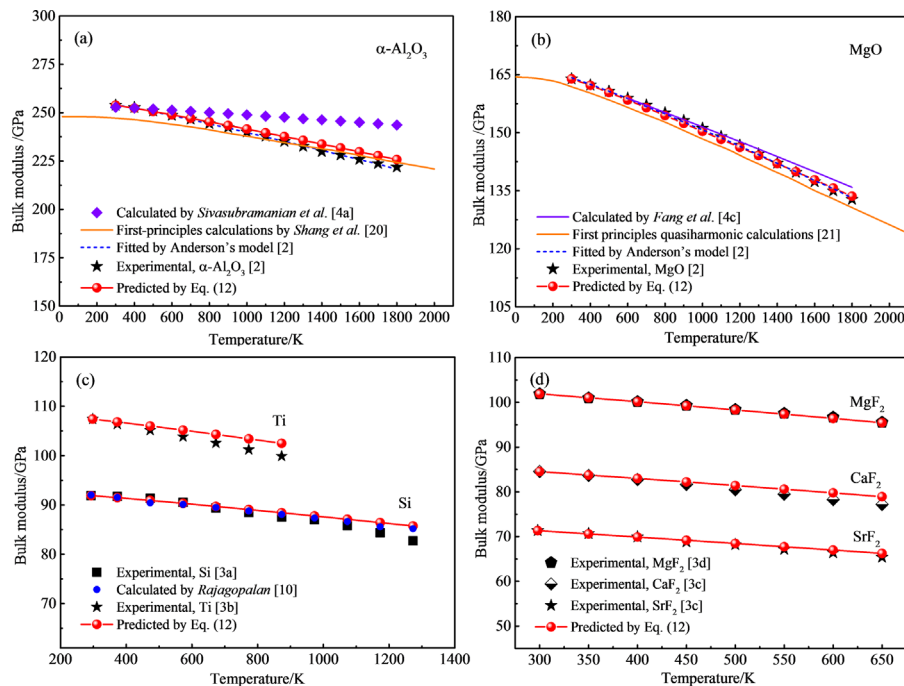


Figure 1. The model predictions and the temperature-dependent adiabatic bulk moduli of α - Al_2O_3 , MgO , Si , Ti , SrF_2 , CaF_2 , and MgF_2 .

1800 K. First principles can offer the good methods to determine the temperature dependent adiabatic bulk moduli of solid single crystals. But the methods rely on the available pseudopotentials and have a large amount of computation especially at elevated temperatures, which could limit their practical applications in the temperature dependent bulk modulus prediction. Rajagopalan's,^[10] Anderson's,^[2] and Fang's model^[4c] give good estimation results, but these models have the adjustable parameter which needs to be determined from the fitting function of sufficient bulk modulus data measured at certain high temperatures in advance. In Figure 1d, the predicted values by Equation (12) are in good agreement with the experimental values of SrF_2 ,^[3c] CaF_2 ,^[3c] and MgF_2 .^[3d] The slight difference between the model predictions and the experimental values of Si (above 1000 K) and Ti (above 750 K) could be resulted from the increase of vacancy concentration with temperature. Generally the thermal vacancy concentration in the crystal increases exponentially with temperature, and according to the study,^[9] this factor could cause the nonlinear reduction of bulk modulus at elevated temperatures. Currently, this factor has not been considered in the present model and could lead to the deviations. Due to the lack of the high temperature spectroscopic data for the seven types of solid single crystals, the model predictions by Aguado et al.^[4f] are not given here for comparison.

The present model shows that, when the temperature range is small enough (ignoring the change in the volume expansion of material), the linear relationship between adiabatic bulk modulus and relative enthalpy indicated by Anderson^[2] can be obtained. Moreover, Equation (12) also indicates that at very high temperatures the adiabatic bulk modulus will decrease nonlinearly with the increase of relative enthalpy. It can explain the nonlinear decrease of bulk modulus experimentally observed

at elevated temperatures, which is generally attributed to the anharmonic effect.^[2] Compared with the existing classical models, the present model has no adjustable parameters and shows good prediction ability, and does not require the experimental measurement of bulk modulus at elevated temperatures in advance. The material parameters used in the present model can be conveniently obtained from experiments, material handbooks and other scholars' studies. As for the parameter $B(T_0)$ at room temperature, for a specific material it can be regarded as a material constant. $B(T_0)$, in essence, depends on the crystalline structures and the constituted chemical bonds. At the microscopic level, bulk modulus can be related to some basic parameters, such as bond length, lattice constant, bond force constant, and cohesive energy.^[22] The bulk modulus $B(T_0)$ at the microscopic level can be given by the empirical formula,^[23] the perturbation theory,^[24] and the chemical bond method,^[25] and so on.

In addition, the variation of crystalline structure, which involves the phase transition, the formation of intrinsic defects, the evolution of initial damages and so on, could occur at elevated temperatures. In the cases where the evolution of structure, defects, and initial damages with temperature is not significant, the effects of these factors on the bulk modulus have been considered through the bulk modulus $B(T_0)$. In the cases where this evolution is significant, the applicable scope of this model is described as follows according to the comparison and discussions in Figure 1. For those solid single crystals which have no solid-state phase transition as temperature increases, the present model can be well used for their bulk modulus prediction below the temperature where vacancies begin to have significant effect on their bulk moduli. For those solid single crystals which have solid-state phase transition as

temperature increases, it is better to apply the present model to predict the bulk moduli below their solid-state phase transition temperatures considering that the corresponding model verifications are conducted just below these temperatures.

4. Conclusions

In summary, a physics-based theoretical model for the temperature-dependent bulk modulus of solid single crystals is developed. Compared with the existing models, the present model has no adjustable parameters, and the model predictions are in good agreement with the temperature-dependent adiabatic bulk moduli of seven types of solid single crystals. This study provides a new and practical method to quantitatively characterize the temperature-dependent bulk modulus of solid single crystals for their high temperature applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under Grant Nos. 11472066, 11672050, and 11727802; the Fundamental Research Funds for the Central Universities under Grant no.106112017CDJQJ328840 and 2018CDPTCG0001/17; the China Postdoctoral Science Foundation Grant no. 2016M592636. We also thank the anonymous reviewers for their helpful comments.

Conflict of Interest

The authors have declared no conflict of interest.

Keywords

bulk modulus, elasticity, modeling, solid single crystals, temperature-dependence

Received: June 14, 2018

Revised: July 19, 2018

Published online:

- [1] a) K. O. Park, J. M. Sivertsen, *J. Am. Ceram. Soc.* **1977**, 60, 537; b) J. Garai, A. Laugier, *J. Appl. Phys.* **2007**, 101, 023514.
[2] O. L. Anderson, *Phys. Chem. Miner.* **1989**, 16, 559.

- [3] a) Y. A. Burenkov, S. P. Nikanorov, *Sov. Phys. Solid State* **1974**, 16, 963; b) E. Fisher, C. Renken, *Phys. Rev.* **1964**, 135, A482; c) L. E. Jones, *Phys. Earth Planet. Inter.* **1977**, 15, 77; d) L. E. Jones, *Phys. Chem. Miner.* **1977**, 1, 179.
[4] a) K. Sivasubramanian, S. Raju, E. Mohandas, *J. Eur. Ceram. Soc.* **2001**, 21, 1229; b) S. Raju, K. Sivasubramanian, E. Mohandas, *Mater. Lett.* **2002**, 54, 13; c) M. X. Fang, Y. E. Pin, Z. T. Yan, *J. Anhui Normal Univ.* **2004**, 27, 29; d) Q. Liu, Q. He, *Int. J. Thermophys.* **2008**, 29, 1491; e) Q. He, Z. T. Yan, *Phys. Status Solidi B* **2001**, 223, 767; f) F. Aguado, V. Baonza, *Phys. Rev. B* **2006**, 73, 024111.
[5] W. Li, F. Yang, D. Fang, *Acta Mech. Sinica* **2010**, 26, 235.
[6] R. Wang, W. Li, B. Ji, D. Fang, *J. Mech. Phys. Solids* **2017**, 107, 365.
[7] W. Li, X. Zhang, H. Kou, R. Wang, D. Fang, *Int. J. Mech. Sci.* **2016**, 105, 273.
[8] C. Kittel, *Introduction to Solid State Physics*, 8th ed., John Wiley & Sons, Inc, Hoboken, US **2005**.
[9] D. L. Ye, J. H. Hu, *Handbook of Practicality Inorganic Thermodynamics*, 2nd ed., Metallurgical Industry Press, Beijing, China **2002**.
[10] Pubchem, <https://pubchem.ncbi.nlm.nih.gov/>, **2017**.
[11] Matweb, <http://www.matweb.com/>, **2017**.
[12] J. A. Dean, *Lange's Handbook of Chemistry*, 15th ed., McGrawHill, Inc, New York, US **1999**.
[13] Microkat, <http://www.microkat.gr/>, **2017**.
[14] O. L. Anderson, D. G. Isaak, in *Mineral Physics & Crystallography: A Handbook of Physical Constants* (Ed: T. J. Ahrens), American Geophysical Union, Washington DC, US **1995**, pp. 64–97.
[15] a) M. Gu, Y. Zhou, L. Pan, Z. Sun, S. Wang, C. Q. Sun, *J. Appl. Phys.* **2007**, 102, 083524; b) Y. Okada, Y. Tokumaru, *J. Appl. Phys.* **1984**, 56, 314.
[16] a) Y. Touloukian, R. Kirby, R. Taylor, P. Desai, *Thermal Expansion – Metallic Elements and Alloys, Thermophysical Properties of Matter (The TPRC Data Series)*, Vol. 12, IFI/ Plenum, New York, US **1975**; b) B. Zhang, X. Li, D. Li, *Calphad* **2013**, 43, 7.
[17] G. Kommichau, H. Neumann, W. Schmitz, B. Schumann, *Cryst. Res. Technol.* **1986**, 21, 1583.
[18] B. Schumann, H. Neumann, *Cryst. Res. Technol.* **1984**, 19, K13.
[19] D. Bailey, F. Calderwood, J. Greiner, O. Hunter, J. Smith, R. Schiltz, *J. Am. Ceram. Soc.* **1975**, 58, 489.
[20] S. L. Shang, H. Zhang, Y. Wang, Z. K. Liu, *J. Phys.: Condens. Mater* **2010**, 22, 375403.
[21] a) Z. Wu, R. M. Wentzcovitch, *Phys. Rev. B* **2009**, 79, 104304; b) R. M. Wentzcovitch, Z. Wu, P. Carrier, *Rev. Mineral. Geochem.* **2010**, 71, 99.
[22] X. Liu, H. Wang, W. Wang, Z. Fu, *Phys. Chem. Chem. Phys.* **2017**, 19, 22177.
[23] M. L. Cohen, *Phys. Rev. B* **1985**, 32, 7988.
[24] P. K. Lam, M. L. Cohen, G. Martinez, *Phys. Rev. B* **1987**, 35, 9190.
[25] S. Y. Zhang, H. L. Li, H. Y. Li, S. H. Zhou, X. Q. Cao, *J. Phys. Chem. B* **2007**, 111, 1304.