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Thermal Grüneisen parameters of CdAl_2O_4 , $\beta\text{-Si}_3\text{N}_4$, and other phenacite-type compounds

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The thermal expansion coefficients of a number of phenacites (Be_2SiO_4 , $\beta\text{-Si}_3\text{N}_4$, $\beta\text{-Sialon}$, $\alpha\text{-LiAlSiO}_4$, Zn_2SiO_4 , CdAl_2O_4 , and Zn_2GeO_4) at temperatures at and above the Debye temperature are analyzed in terms of the thermal Grüneisen parameter γ . The phenacites have γ values intermediate between adamantane crystals and quartz. Values of γ between 0.3 and 0.7 are found. A useful correlation exists between γ and the average volume per anion bond W . Values of γ approaching zero occur for sufficiently large values of W .

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I. INTRODUCTION

A number of phenacite-type compounds such as $\beta\text{-Si}_3\text{N}_4$,¹⁻⁶ $\beta\text{-Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$,^{2,3,6,7} Zn_2GeO_4 ,^{8,9} and Zn_2SiO_4 ,⁸ have been reported to have an extremely small thermal expansion. In comparison to this, two phenacite-type compounds, Be_2SiO_4 ¹⁰⁻¹² and $\alpha\text{-LiAlSiO}_4$,¹³ have been reported to have a much larger thermal expansion. Recent expansion data on several other phenacites, as well as the published literature, are analyzed in terms of the high temperature thermal Grüneisen parameter γ . Some useful correlations are found between γ , the average coordination number, and the average volume per atom.

II. EXPERIMENTAL PROCEDURE

Recently Huseby, Slack, and Arendt reported¹⁴ new data on the thermal expansion of three phenacite structure compounds at room temperature and above. In this work,¹⁴ the thermal expansion coefficients are defined, the experimental procedures for CdAl_2O_4 , $\beta\text{-Si}_3\text{N}_4$, and $\beta\text{-Sialon}$ are detailed, and the dilatometer curves are presented. The volume thermal expansion coefficient $\beta(T)$ is defined¹⁴ as the

logarithmic derivative of the volume with respect to temperature:

$$\beta(T) = \frac{d \ln V}{dT}.$$

The thermal expansion anisotropy for the i th axis of the expansion ellipsoid is defined¹⁴ as

$$A_i(T) = \beta(T) - 3\alpha_i(T),$$

where $\alpha_i(T)$ is the linear thermal coefficient along the i th axis. The CdAl_2O_4 had the phenacite structure of Colin and Thery,^{15(a)} not the spinel structure of Hahn *et al.*^{15(b)} The Si_3N_4 was $\beta\text{-Si}_3\text{N}_4$ with the phenacite structure type,^{16,17} not the $\alpha\text{-Si}_3\text{N}_4$ structure.¹⁸

III. RESULTS

The volume thermal expansion coefficients of $\beta\text{-Si}_3\text{N}_4$, CdAl_2O_4 , and $\beta\text{-Sialon}$ ($\text{Si}_{2.6}\text{Al}_{3.4}\text{O}_{3.4}\text{N}_{4.6}$) are given in Figs. 1 and 2. These were computed from three times the average

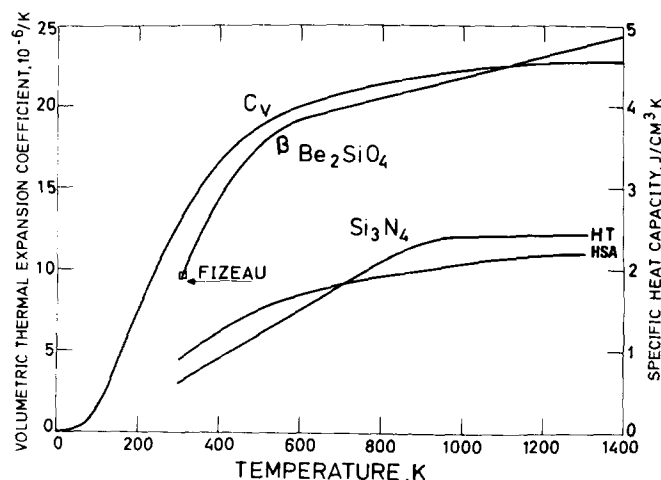


FIG. 1. Specific heat capacity and volumetric thermal expansion coefficient vs temperature for Be_2SiO_4 . The square datum is from Fizeau, 1888 (see Ref. 12). The curves for $\beta\text{-Si}_3\text{N}_4$ are the volumetric thermal expansion coefficient from the present study, HSA, Ref. 14, and from Henderson and Taylor, Ref. 1.

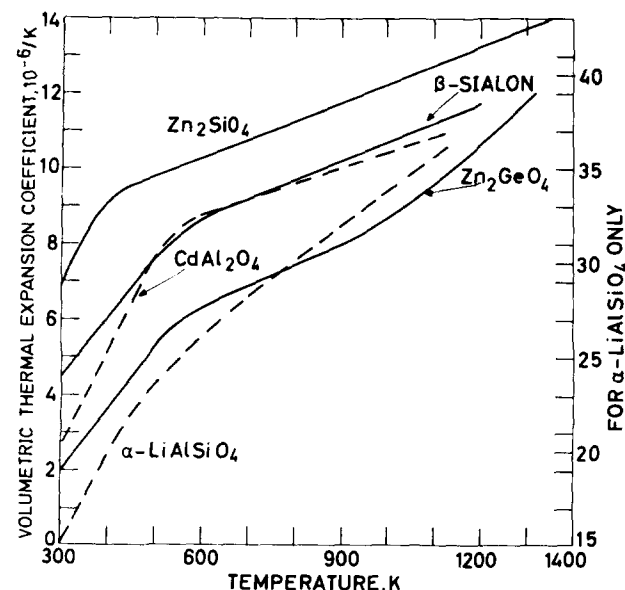


FIG. 2. Volumetric thermal expansion vs temperature for five phenacites. The CdAl_2O_4 and $\beta\text{-Sialon}$ are from the present study. The other curves are best estimates of data from the literature, Refs. 8, 9, 13, 19-21. The scale for $\alpha\text{-LiAlSiO}_4$ appears on the right side.

TABLE I. Volumetric thermal expansion coefficients and expansion anisotropy vs temperature.

Material	$\beta(T), 10^{-6}/\text{deg}$			$A_a, 10^{-6}/\text{deg}$			Reference	
	300 K	650 K	1000 K	300 K	650 K	1000 K	β	A
Be_2SiO_4	9.0	19.5	21.8	0.8			10	12
$\beta\text{-Si}_3\text{N}_4$	4.4	8.7	10.4	1.1	0.7	0.2	<i>P</i>	1
$\alpha\text{-LiAlSiO}_4$	15.1	27.3	33.9	-7.1	0.10	1.0	13	13
Zn_2SiO_4	6.9	10.5	12.3	>0	>0	~0.0	8	8
CdAl_2O_4	2.6	9.0	10.5				<i>P</i>	
Zn_2GeO_4	2.0	6.6	8.7	3.0	0.7	0.7	8	8
$\beta\text{-Sialon}$	2.6	9.0	10.7				<i>P</i>	

P = Present work.

linear coefficient. The linear coefficients were determined from the slopes of the dilatometer curves at the specified temperatures. All three materials have similar and small thermal expansion coefficients. Values of $\beta(T)$ are given in Table I at 300, 650, and 1000 K. In addition, data in the literature for four other phenacite-type compounds are given. Some additional expansion data¹⁹⁻²¹ are available for Zn_2SiO_4 (willemite). These confirm the low volume expansion coefficient below 400 K shown in Fig. 3 for Zn_2SiO_4 , where the data of Wen *et al.*⁸ are not very reliable.²⁰

In addition, some data on the expansion anisotropy are available, as shown in Table I. The results show that although the anisotropy is considerable at room temperature, the crystals are nearly isotropic at high temperatures. Note that A_a at 300 K for $\alpha\text{-LiAlSiO}_4$ is negative while the others are positive. The present interest is not in A_i , hence we will be

concerned almost entirely with $\beta(T)$, its magnitude and dependence on temperature. We are especially interested in why the phenacite compounds have such a large range in expansion coefficients, and how to explain the low expansion coefficients of Si_3N_4 and Zn_2GeO_4 .

IV. DISCUSSION

A. Debye temperatures and bulk moduli

The interpretation of thermodynamic properties such as thermal expansion becomes easiest at temperatures near to or above the Debye temperature θ . Hence we would like to know the values θ for all of the phenacites. Heat capacity data exist for Be_2SiO_4 ,²² Zn_2SiO_4 ,^{23,24} and Si_3N_4 .^{25,26} The data of Refs. 24 and 25 do not appear to be too reliable and are disregarded. The results of Refs. 22, 23, and 26 have been converted to values of the Debye temperature, as shown in Fig. 3. Many crystals exhibit a minimum of a $\theta(T)$ vs T plot, as do Be_2SiO_4 and Zn_2SiO_4 . The minimum for Be_2SiO_4 is at 65 K, or at $T/\theta_0 = 0.057$. The minimum in Zn_2SiO_4 is estimated.

It is possible to calculate the value of θ at absolute zero if the elastic constants are known at this temperature. No such data have been found in the literature. However, room temperature data for the bulk modulus B and Poisson's Ratio σ can be used²⁷ to estimate θ_0 . This was done for Si_3N_4 using $B = 278$ GPa from Srinivasa *et al.*²⁸ and $\sigma = 0.222$ from Fate.²⁹

Here and in subsequent discussions, we shall be using the isothermal values of B , not the adiabatic values. Also, when single-crystal elastic constants are available, we shall use the Voigt-Reuss-Hill³⁰ average for B . For Si_3N_4 , we calculate $\theta_0 = 1145$ °K. This value is given in Table II, as well as θ_0 values for the other compounds computed from the estimated B values by assuming that $\sigma = 0.222$ for all phenacites.

For the other compounds, no B values were found in the published literature. There is a value²⁰ for the Young's Modulus of $(\text{Zn}_{0.65}\text{Mg}_{0.35})_2\text{SiO}_4$ ceramic. If $\sigma = 0.222$, the calculated value of B is 45 GPa. This value appears to be too low compared to the θ vs T curves of Fig. 1. Therefore a method of estimating B was devised. The B of ZnO is $B = 143$ GPa, as calculated from single-crystal elastic constants.³¹ Similar data exist for BeO ,³² LiGaO_2 ,³³ $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$,³⁴ Stishovite- SiO_2 ,³ rutile- GeO_2 ,³⁶ and ZrSiO_4 .³⁷ These values of B are given in Table III. The B value for the SiO_4 tetrahedron when it is fixed in space and does not rotate under compres-

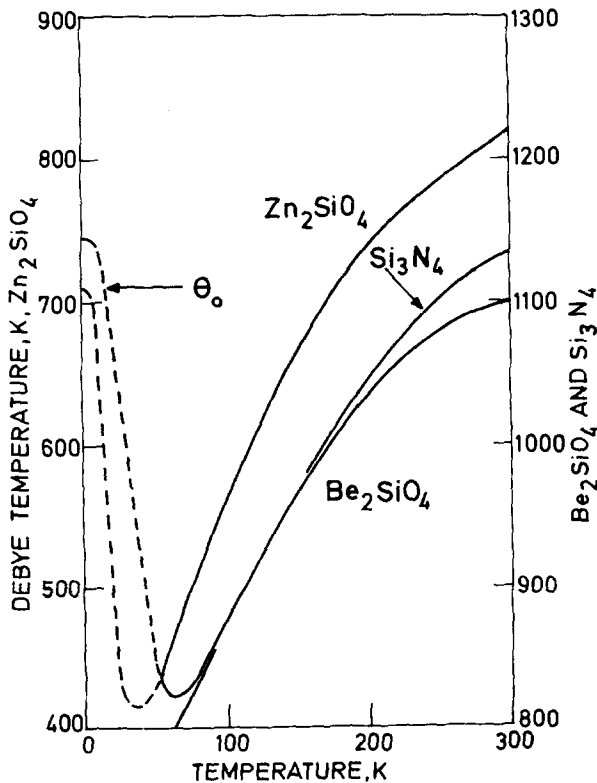


FIG. 3. Debye temperature as a function of temperature based on heat capacity data, solid curves. The dashed curves indicate the expected behavior in order to agree with computed θ_0 values.

TABLE II. Properties of phenacite structure compounds.

Compounds	δ	\bar{M}	ρ	B	θ_0	θ_∞	$-\frac{\partial \ln B}{\partial T}$	W	γ_θ
Be ₂ SiO ₄	2.060	15.73	2.988	224	1145	1100	1.0	5.096	1.02
β -Si ₃ N ₄	2.183	20.04	3.195	278	1160	1140	1.0	6.072	0.72
β -Sialon	2.222	20.26	3.063	230	1060		1.0	6.403	0.62
α -LiAlSiO ₄	2.249	18.00	2.626	75	650		1.5	6.637	0.56
Zn ₂ SiO ₄	2.318	31.83	4.242	155	710	820	1.5	7.266	0.52
Cd ₂ AlO ₄	2.368	32.91	4.119	140	605		2.0	7.739	0.39
Zn ₂ GeO ₄	2.367	38.19	4.778	150	645		2.0	7.743	0.31
Li ₂ WO ₄	2.388	37.39	4.559					7.940	

δ^3 = average volume occupied by one atom, in 10^{-24} cm³ (δ in Å).

\bar{M} = average atomic mass, g.

ρ = x-ray density at room temperature, g/cm³.

B = isothermal bulk modulus at room temperature, GPa.

θ_0 = Debye temperature at absolute zero estimated from B , ρ , and σ at room temperature, in K.

θ_∞ = Debye temperature at high temperature calculated from specific heat capacity, in K.

$\partial \ln B / \partial T$ = temperature dependence of B , estimate, in $10^{-4}/K$.

W = average volume per anion bond = $7\delta^3/12$.

γ_θ = dimensionless Grüneisen parameter at $T = \theta_\infty$.

sion has been deduced by Hazen and Finger³⁷ from the data on ZrSiO₄. It is $B = 227$ GPa. The bulk modulus of crystals of α -quartz, SiO₂, is much less³⁸ at $B = 37.4$ GPa. It is clear that internal molecular group rotations, which occur readily in α -SiO₂ and in β -SiO₂,³⁹ drastically affect the value of B . In the following development, we shall assume that no such rotations take place in the phenacite structure under compression. This appears to be a reasonable assumption for this crystal structure.

A crystal of Zn₂SiO₄ can be thought of as being composed of individual ZnO₄ and SiO₄ tetrahedral group in the ratio 2:1. The ratio of the volume fraction of ZnO₄ to SiO₄ is given by

$$\text{Volume Ratio} = 2 \left[\frac{r(\text{Zn}) + r(\text{O})}{r(\text{Si}) + r(\text{O})} \right]^3, \quad (1)$$

where r_i are the ionic radii of the various ions as given by Shannon and Prewitt.⁴⁰ The result is that Zn₂SiO₄ is 78.0% by volume ZnO₄ groups. Similar arguments apply to the other compounds. The crystal is a sum of two volume components. The composite bulk modulus can be derived from the pressure effects on the volumes of the several components.

TABLE III. Bulk modulus values for crystals and molecular groups.

Crystal	Literature		Group	Derived	
	B (GPa)	Ref.		B (GPa)	Ref.
SiO ₂ -Stishovite	344	35	SiO ₄	227	37
GeO ₂ -rutile	258	36	AlO ₄	200	P
α -Al ₂ O ₃	250	44	GeO ₄	170	P
ZrSiO ₄	235	37	CdO ₄	105	P
BeO	224	32			
Be ₃ Al ₂ Si ₆ O ₁₈	180	34			
ZnO	143	31			
CdO	108	43			
LiGaO ₂	60.3	33			

P = Present work.

For example, in Zn₂SiO₄, this is

$$\begin{aligned} V_{\text{TOT}} &= 2V(\text{ZnO}_4) + V(\text{SiO}_4), \\ \frac{\partial V_{\text{TOT}}}{\partial P} &= \frac{2\partial V(\text{ZnO}_4)}{\partial P} + \frac{\partial V(\text{SiO}_4)}{\partial P}, \\ \frac{1}{B_{\text{TOT}}} &= \frac{1}{V_{\text{TOT}}} \frac{\partial V_{\text{TOT}}}{\partial P} = \frac{2V(\text{ZnO}_4)/V_{\text{TOT}}}{B(\text{ZnO}_4)} \\ &\quad + \frac{V(\text{SiO}_4)/V_{\text{TOT}}}{B(\text{SiO}_4)}. \end{aligned} \quad (2)$$

The $B(\text{ZnO}_4)$ is assumed to be same as B of ZnO. Thus, for Zn₂SiO₄, we obtain $B = 155$ GPa (see Table II). This is much larger than the value found for ceramic (Zn-Mg)₂SiO₄. Similar calculations for Be₂SiO₄, Zn₂GeO₄ give the B values in Table II. Note that the estimated B value of Be₂SiO₄ is similar to but larger than that measured³⁴ for Be₃Al₂Si₆O₁₈, which also has an open-channel, hexagonal structure (see Table III). The compound α -LiAlSiO₄ is slightly more complicated. First, we calculate the volume fractions of LiO₄, GaO₄, and SiO₄ in the phenacite LiGaSiO₄. The Li-Ga-O fraction is assumed to have the same bulk modulus³³ as the adamantane crystal LiGaO₂. Combining this with an SiO₄ group gives for LiGaSiO₄ a value of $B = 73.1$ GPa.

We now use the approximation⁴¹ that for compounds with the same crystal structure, the product of bulk modulus and molar volume is constant. Since the molar volume⁴² of LiAlSiO₄ is 97% of that of LiGaSiO₄, its estimated bulk modulus is $B = 75$ GPa (see Table II).

For CdAl₂O₄, we first estimate B for CdO₄ groups from the B of ZnO and the expected⁴⁰ molar volume ratio of

$$\left[\frac{r(\text{Cd}) + r(\text{O})}{r(\text{Zn}) + r(\text{O})} \right]^3 = 1.36. \quad (3)$$

Thus for CdO₄, we obtain $B = 143/1.36 = 105$ GPa. For CdO with the rocksalt structure, the measured⁴³ value is $B = 108$ GPa. For AlO₄ groups, we assume a value of b midway between those for GeO₄ and SiO₄, and obtain $B = 200$ GPa for AlO₄. For α -Al₂O₃, the value⁴⁴ is $B = 250$ GPa,

where there are AlO_6 groups. For CdAl_2O_4 , the result is $B = 140$ GPa (see Table II).

B. Heat capacities

In Table II and Fig. 3, the θ_0 values for Be_2SiO_4 , Si_3N_4 , and Zn_2SiO_4 are seen to be close to the high temperature Debye temperature θ_∞ . Thus we make the assumption that this is true for all of the phenacites. Then, at 300 K and above, we can calculate the specific heat capacity as a function of temperature for all of the compounds. Note that at the very highest temperatures $T \gg \theta$, the specific heat is assumed to be just the Dulong-Petit value of $C_{V_\infty} = 174.7$ J/mole K, since there are 7 atoms per molecule. Thus, for $T > 300$ K, we know that C_V , the specific heat capacity at constant volume, for Be_2SiO_4 lies between $0.53 \leq C_V/C_{V_\infty} < 1.00$. Since Be_2SiO_4 has the highest Debye temperature of all the compounds, then the C_V/C_{V_∞} range for all of the others will be less. For CdAl_2O_4 , we find that for $T > 300$ K, one obtains $0.82 \leq C_V/C_{V_\infty} < 1.00$. These results mean that although the θ_∞ values are only approximate, they may be accurate to ± 50 K, the error in the estimated heat capacity will be small. For Be_2SiO_4 , the error at 300 K would be $\pm 5\%$, for the others it would be less. The error also decreases with increasing temperature, such that at $T = \theta_\infty$ it is less than $\pm 0.4\%$ for any of the compounds.

C. Grüneisen parameters

The thermodynamic Grüneisen parameter γ at temperature T is defined⁴⁵ as

$$\gamma(T) = \beta B V_m / C_V, \quad (4)$$

where β is the volume thermal expansion coefficient, B is the isothermal bulk modulus, C_V the isochoric specific heat capacity per mole, and V_m the molar volume. In general, for a noncubic crystal, γ is a tensor quantity.⁴⁶ However, if we use the volume coefficients β and B , we obtain the directionally averaged γ . Furthermore, at high temperatures near $T = \theta$, the anisotropy in α is very small, hence all the γ_i values will be similar. Thus Eq. (4) yields quite acceptable values of $\gamma(\theta_\infty)$.

In order to calculate $\gamma(T)$, we have used $\beta(T)$ values measured in the present experiment, as well as values taken from the literature. These are plotted in Figs. 1 and 2, and some values are given in Table I. Some liberties have been taken, using our best judgment, in smoothing irregularities in the literature data so that the $\beta(T)$ curves do not possess obscure anomalies. The original literature should be consulted for the raw data. For $\beta\text{-Si}_3\text{N}_4$, the present data in Fig. 1 (by HSA) was used to compute $\gamma(T)$. The results of Henderson and Taylor,¹ curve *HT*, are shown for comparison.

To a good approximation, the temperature dependence of γ is produced by the temperature dependence of C_V and β while V_m and B are nearly independent of temperature. For Si_3N_4 it was found²⁹ that B decreases slowly with increasing temperature at a rate of approximately

$$\frac{\partial \ln \beta}{\partial T} = -1.0 \times 10^{-4} / \text{K}. \quad (5)$$

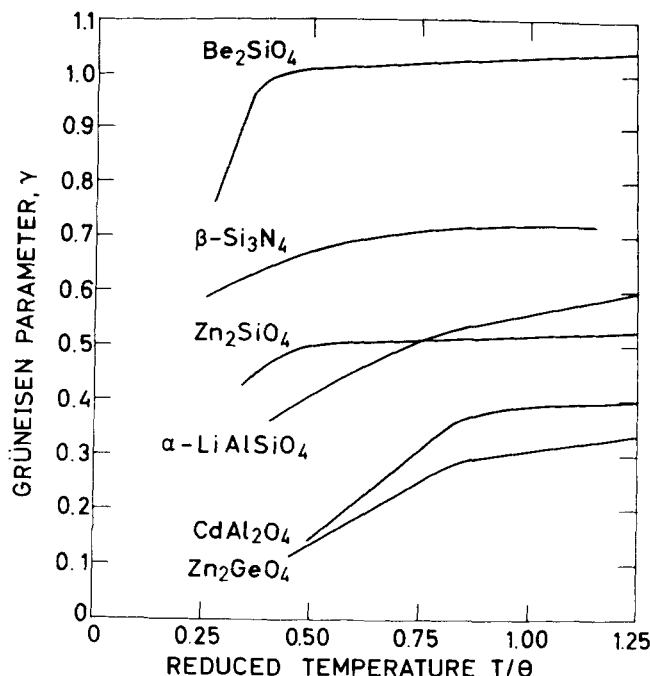


FIG. 4. Grüneisen parameter vs reduced temperature for six different phenacites.

Such behavior is typical of most oxides for $T > \theta/10$, and values of up to $-2 \times 10^{-4}/\text{K}$ are found. Hence we have, somewhat arbitrarily, assigned values for $(\partial \ln B / \partial T)$ to the compounds in Table II. The values of $-2 \times 10^{-4}/\text{K}$ were given to those compounds with the lower Debye temperature.

With the above conditions on C_V , β , and B we have computed $\gamma(T)$. The results are plotted in Fig. 4 vs T/θ . In general, at temperatures near $T = \theta_\infty$ the value of γ is nearly independent of temperature. We have chosen to select $\gamma(\theta_\infty) = \gamma_\theta$ as a representative high-temperature value. These results are given in Table II. Notice that γ_θ decreases as one proceeds downward through the table.

D. Volume dependence of γ_θ

The most striking behavior of the γ_θ values is that they are not the same for all of the phenacites, and that the range of values is much larger than is usually found⁴⁶ for other groups of isostructural compounds. The phenacites have 4-coordinated cations and 3-coordinated anions, i.e., (4,3). Thus they are intermediate between the adamantane crystals, which are (4,4), and quartz, which is (4,2). The γ values for the (4,4) crystals lie between⁴⁶ $+0.9 \geq \gamma \geq +0.46$, while α -quartz has a positive^{44,47} γ value at 300 K, but β -quartz has a negative⁴⁸ γ value in its region of existence above 846 K. Thus, on the average, at high temperatures, quartz has $\gamma \sim 0$. So we might expect the phenacites to have intermediate γ_θ values.

Blackman^{49,50} has pointed out that crystals with an open crystal structure can have certain vibrational modes with negative γ values, and that in special cases, the limiting value of γ at very high temperatures γ_∞ might also be negative. This is apparently the case for β -quartz. The exact be-

havior appears to depend on the availability of open spaces inside the crystal lattice, such that for some directions of motion, certain atoms will find very weak repulsive forces. This is true in phenacites. There are open channels^{1,51-53} running parallel to the c axis. The triply coordinated oxygen atoms on the walls of these channels can move easily in the a - b plane with very weak repulsive forces. Thus we expect that this "anisotropic thermal motion"⁵⁴ should tend to produce low values of γ .

In searching for a correlation of our γ_θ values with other crystallographic parameters, we have found that it correlates well with δ^3 , the average volume per atom in the crystal. We define an average volume per oxygen bond W as follows for phenacites

$$W = \frac{7\delta^3}{4\eta} \quad (6)$$

The average volume per molecule is $7\delta^3$. Each molecule has 4 oxygen atoms, hence the average volume available for each oxygen atom is $7\delta^3/4$. Each oxygen is bonded to 3 cations, hence $\eta = 3$. Thus

$$W = 7\delta^3/12. \quad (7)$$

The same is true for Si_3N_4 , where $\eta = 3$ for nitrogen. A plot of γ_θ vs W is shown in Fig. 5. Note that γ_θ decreases essentially linearly with increasing W . In Fig. 5, we estimate that our calculated γ_θ values may be inaccurate to $\pm 10\%$ (or perhaps $\pm 20\%$), hence the error bars indicate the $\pm 10\%$ uncertainty. Within this accuracy, a straight line fit is certainly valid. The point for $\beta\text{-Si}_3\text{N}_4$ also fits the curve for the oxides.

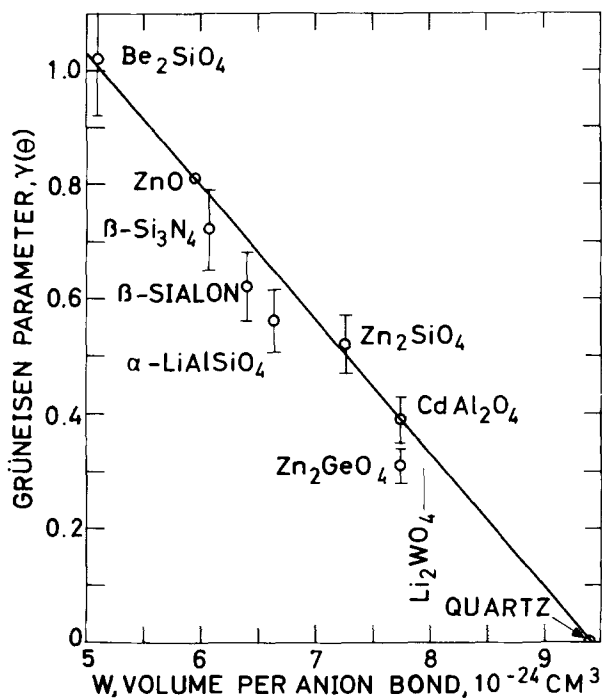


FIG. 5. Grüneisen parameter at $T = \theta$ as a function of W , the volume per anion bond for nine different compounds. The line for Li_2WO_4 shows the maximum value of W for any known phenacite.

TABLE IV. Some properties of adamantine and quartz crystals.

Crystal	B (GPa)	η	W	γ_∞	Ref.
BeO	224	4	3.484	1.27	32,44,46
ZnO	143	4	5.949	0.814	31,44
$\alpha\text{-SiO}_2$	37.4	2	9.418	0.0	39,48
$\beta\text{-SiO}_2$	56.3	2	9.909		39,48

B = isothermal bulk modulus at room temperature, GPa.

η = coordination number of anions.

W = average volume per anion bond, 10^{-24} cm^3 .

γ_∞ = Grüneisen parameter at high temperature, $T > \theta$.

E. Phenacites and related compounds

We can carry the comparison of phenacites with their parent compounds a bit further. Table IV gives the known γ_∞ values for the parent compounds of Be_2SiO_4 and Zn_2SiO_4 . By using the same parameter W , we show how the γ values compare with those of the phenacites. The general definition of W is

$$W = (N_A + N_C)\delta^3/\eta N_A, \quad (8)$$

where N_A = number of anions and N_C = number of cations in the molecule. Table IV gives the W values calculated from Eq. (13). For quartz, we have plotted $\gamma = 0$ at the W value for $\alpha\text{-SiO}_2$ (low quartz) in Fig. 5. The straight line has the form

$$\gamma = \Gamma_\infty [1 - (W/W_0)], \quad (9)$$

with $\Gamma_\infty = 2.91$ and $W_0 = 9.45 \times 10^{-24} \text{ cm}^3$. The points for ZnO and BeO (not shown) fall close to this line. Thus the γ_θ values follow from the γ_θ values of the parent compounds in a very simple fashion. The fundamental reasons why Eqs. (8) and (4) work so well may need further explanation later. For the present, it is clear that as the internal lattice volume increase, the average γ value decreases in a linear fashion. The "anisotropic thermal motion" of the oxygen or nitrogen in the phenacites must become a larger and larger effect as the crystal volume is expanded by larger ions. Clearly, W_0 is the volume at which the lattice finally balances the two effects of atomic bond expansion and anisotropic thermal motion. The SiO_4 tetrahedra are readily rotated in quartz and their rotation is responsible for the α - β transition. The significance of Γ_∞ is less clear. It appears to be an upper bound on the γ_∞ values for all oxides.

F. Application of results

The highest expansion coefficient of all the phenacites studied was that of $\alpha\text{-LiAlSiO}_4$. Its γ_θ value clearly fits the curve in Fig. 5. Hence, its high β value is caused not by an anomaly in γ , but by the very low bulk modulus for the LiO_4 groups. The phenacite with the largest W value known is Li_2WO_4 . Its γ_θ value should be 0.34. However, its expansion coefficient is apt to be even larger than that of $\alpha\text{-LiAlSiO}_4$ because its bulk modulus will be lower.

The lowest β at high temperatures is found for Zn_2GeO_4 , which has a moderately low γ value and a moderately high B value. The low expansion of Si_3N_4 is caused primarily by its very large bulk modulus, in spite of a γ value

very similar to that of ZnO. We also expect Ge_3N_4 with $W = 7.17 \text{ \AA}^3$ to have a lower β at high temperatures than Si_3N_4 . Hence it might prove useful.

In Fig. 5, both oxides and nitrides appear to follow the same β vs W curve. Hence β -Sialon should fall on the curve, since it is an oxynitride. From the B values in Table III, we have estimated that for the present β -Sialon composition of $0.433 (\text{Si}_3\text{N}_4) + 0.567 (\text{Al}_3\text{O}_3\text{N})$, the value of B is 230 PGa (see Table II). As $\text{Al}_3\text{O}_3\text{N}$ is added to the β - Si_3N_4 , the lattice expands, W increases, and γ_θ decreases. However, B also decreases because the B of the AlO_4 group is significantly less than that of the SiN_4 group. The increasing γ and decreasing B effects nearly compensate. Thus, as our results in Table I show, the thermal expansion at high temperatures of the β -Sialon is slightly larger than that of β - Si_3N_4 . At the maximum aluminum content of approximately $\text{SiAl}_2\text{O}_2\text{N}_2$, it is estimated that the β at $T = \theta$ will be about 6% larger than that of β - Si_3N_4 .

V. CONCLUSIONS

The volumetric thermal expansion coefficients of the phenacites have been converted to values of $\gamma(T)$ from estimates of the bulk modulus and specific heat capacity. At $T = \theta$, the γ values obey a simple relationship $\gamma = \Gamma_\infty [1 - (W/W_0)]$, and show that the phenacites behave in a manner intermediate between that of the adamantite structure and the quartz structure. The average volume per anion bond W is used as the scaling parameter.

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