

Calculation of the anisotropic thermal parameters of the atoms of α -quartz

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The development of methods for modeling the structure of crystals on the basis of the construction of the many-parameter Born-Mayer-Morse potential makes it possible to calculate with sufficient accuracy various physical characteristics of crystals, such as the elastic and dielectric constants, piezoelectric coefficients, etc.¹⁻³ The calculation of the structural characteristics and the elastic, dielectric, and piezoelectric constants and coefficients of thermal expansion by minimization of the energy of atomization of the crystal by the penalty-functions method has shown good agreement with experimental data for the structure of α -SiO₂ (space group P3₁21; $a = 4.9134$, $c = 5.4052$ Å) (Ref. 4).

In the present paper we give the results of a calculation of a subtle characteristic of the α -SiO₂ crystal, specifically, the anisotropy of the thermal vibrations of the atoms, which is related to the mean-square deviation of their centers from the equilibrium position

$$\overline{\Delta u^2} = \overline{u^2} - \bar{u}^2. \quad (1)$$

We shall consider a range of temperatures such that $kT \ll \Phi_0$ (Φ_0 is the potential energy of the interatomic interaction under equilibrium conditions), but which at the same time are high enough to be able to use the classical Maxwell-Boltzmann distribution

$$\overline{u^2} = \frac{\int_{-\infty}^{+\infty} u^2 \exp(-\Phi/kT) du}{\int_{-\infty}^{+\infty} \exp(-\Phi/kT) du}. \quad (2)$$

Expanding $\Phi(u)$ in a series near the minimum point $u = u_0$ and restricting the treatment to terms up to and including those of third order gives

$$\Phi(u) = \Phi_0 + \alpha(u - u_0)^2 + B(u - u_0)^3 + \dots, \quad (3)$$

$$\text{where } \alpha = \frac{1}{2} \left(\frac{d^2 \Phi}{du^2} \right)_0, \quad \text{and } B = \frac{1}{6} \left(\frac{d^3 \Phi}{du^3} \right)_0.$$

The exponent can be represented in the form

$$\exp(-\theta \Phi) = \exp(-\theta \Phi_0) \exp[-\alpha \theta (u - u_0)^2] [1 - B \theta (u - u_0)^3], \quad (4)$$

$$\theta = (kT)^{-1}.$$

Replacing the variables $x = u - u_0$ in Eq. (2) and using Eq. (4), we find

$$\overline{u^2} = \frac{\int_{-\infty}^{+\infty} \exp(-\theta \alpha x^2) (x + u_0)^2 dx - B \theta \int_{-\infty}^{+\infty} \exp(-\theta \alpha x^2) x^3 (x + u_0)^3 dx}{\int_{-\infty}^{+\infty} \exp(-\theta \alpha x^2) dx - B \theta \int_{-\infty}^{+\infty} \exp(-\theta \alpha x^2) x^3 dx}. \quad (5)$$

Since for any odd value of n we have $\int_{-\infty}^{+\infty} x^n \exp(-\theta \alpha x^2) dx = 0$, it follows that

$$\begin{aligned} \int_{-\infty}^{+\infty} x^n \exp(\alpha x^2) dx &= 0, \quad \int_{-\infty}^{+\infty} \exp(-\theta \alpha x^2) dx = \frac{\pi^{1/2}}{(\theta \alpha)^{3/2}}, \\ \int_{-\infty}^{+\infty} x^4 \exp(-\theta \alpha x^2) dx &= \frac{3\pi^{1/2}}{4(\theta \alpha)^{5/2}}, \end{aligned} \quad (6)$$

so that

$$\overline{u^2} = u_0^2 - \frac{1}{2\theta \alpha} - \frac{3}{2} \frac{u_0 B}{\theta \alpha^2}. \quad (7)$$

Similarly

$$\overline{u^2} = u_0^2 - \frac{3}{2} \frac{u_0 B}{\alpha^2 \theta} + \frac{9B^2}{16\alpha^2 \theta}. \quad (8)$$

Substituting Eqs. (7) and (8) in Eq. (1), we obtain

$$\overline{\Delta u^2} = \frac{kT}{2\alpha} - \frac{9B^2 k^2 T^2}{16\alpha^4}. \quad (9)$$

The parameters of the potential Φ were previously calculated⁴ by minimizing the energy of atomization by varying the structural and energetic parameters within previously specified limits. A knowledge of the potential makes it possible to calculate the second and third derivatives in any direction, and by means of Eq. (9) to obtain the components of the tensor of the mean-square deviations.

On the other hand, the quantity $\overline{\Delta u^2}$ can be calculated if the related thermal parameters of the atoms are known; these parameters are determined by refining the structure by the method of least squares using the structure factors obtained from x-ray diffraction data. The expression for the structure factor contains the temperature factor of the atom k

$$T_k(\mathbf{H}) = \exp[-W_k(\mathbf{H})],$$

where $\mathbf{H}$ is the reciprocal lattice vector. If it is assumed that the displacements of the atom in the thermal motion are identical, i.e., are isotropic, it follows that

$$W_k = \frac{8\pi^2 \sin^2 \theta}{\lambda^2} u_k^2.$$

The refinement of the structure of the MLS involves the quantity $B_k = 8\pi^2 u_k^2$, called the isotropic temperature factor. If the atom undergoes anisotropic thermal vibrations, a tensor with six independent components is used in the harmonic approximation for the description of the thermal motion, and the temperature factor is written as

$$T(\mathbf{H}) = \exp[-2\pi^2 (h^2 a^{*2} u_{11} + k^2 b^{*2} u_{22} + l^2 c^{*2} u_{33} + hka^* b^* u_{12} + hla^* c^* u_{13} + klb^* c^* u_{23})], \quad (10)$$

where h , k , and l are the Miller indices, a^* , b^* , and c^* are the basis vectors in reciprocal space, and u_{ij} are the components of the tensor of the vibrations of the atoms in the crystal.

TABLE I. Calculated and Measured⁵⁻⁸ Coordinates and Anisotropic Thermal Properties of the Si and O atoms

Characteristic	Calculated	Measured			
		[5]	[6]	[7]	[8]
Si					
x	-0.463	-0.4699(1)	0.4697(2)	0.4698(3)	0.4705(3)
y	x			x	
z	1/3			1/3	
$u_{11} \cdot 100, \text{\AA}^2$	0.643	0.66(1)	0.65(4)	0.48(6)	0.45(4)
u_{22}	0.559	0.59(2)	0.54(5)	0.27(7)	0.25(5)
u_{33}	0.590	0.60(1)	0.59(3)	0.63(6)	0.72(4)
u_{23}	-0.097	-0.03(1)	-0.02(3)	0.04(4)	-0.02(4)
O					
x	0.413	0.4141(2)	0.4125(4)	0.4145(8)	0.4152(7)
y	0.275	0.2681(2)	0.2662(4)	0.2662(7)	0.2678(6)
z	0.121	0.1188(1)	0.1188(2)	0.1189(4)	0.1184(4)
$u_{11} \cdot 100, \text{\AA}^2$	1.627	1.56(4)	1.63(9)	1.28(16)	1.31(10)
u_{22}	1.293	1.15(3)	1.27(8)	1.05(14)	0.74(8)
u_{33}	1.295	1.19(3)	1.28(7)	1.28(12)	1.33(9)
u_{12}	0.985	0.92(3)	0.97(8)	0.69(12)	0.78(8)
u_{13}	-0.283	-0.29(3)	-0.27(7)	-0.35(12)	0.37(8)
u_{23}	-0.513	-0.46(2)	-0.43(6)	-0.44(10)	0.49(6)

Table I gives the results of the calculation of the components of the tensor u_{ij} using the potential of the interatomic interaction, together with the data obtained in highly accurate x-ray diffraction studies⁵⁻⁷ for α -SiO₂. It can be seen from Table I that the agreement between the calculated and measured values of u_{ij} is satisfactory.

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