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Anisotropic thermal expansion in wurtzite-type crystals

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The temperature dependence of the lattice parameters of six wurtzite-type crystals, BeO, AlN, GaN, ZnO, CdSe, and CdS, has been measured by X-ray powder diffractometry. The thermal expansion changes nonlinearly with temperature and is anisotropic; the expansion along the *a*-axis is larger than that along the *c*-axis (more than 50% larger in ZnO, CdS and CdSe), resulting in a decrease of the *c*/*a* ratio with increasing temperature. The calculated Grüneisen parameters range between 0.27 and 1.45 and have a positive correlation with the bulk moduli. The anisotropic thermal expansion is associated with the anisotropies of both elasticity and anharmonicity.

1. Introduction

The thermal expansion of a crystal often has a crucial effect on material processing. A common effect is thermal-stress-induced cracking in the material during cooling from high temperatures. A difference in the thermal expansion coefficients of two crystals incoherently joined at a boundary can induce a failure in one of the crystals when subjected to heat treatment. When two crystals are coherently attached, heat treatment can produce dislocations at the boundary if the thermal expansion coefficients of the two crystals differ significantly. Thus, knowledge of the thermal expansion properties of crystalline matter is important for material processing.

The thermal expansion of a crystal reflects the anharmonicity of the crystalline lattice. For crystals with a noncubic symmetry, the thermal expansion is generally anisotropic due to the anisotropic nature of the crystal bonding. Hence, it is of interest from a physical point of view to investigate anisotropic thermal expansion of noncubic crystals.

In the present study, we investigated the temperature dependence of lattice parameters at high temperatures for six wurtzite-type crystals and examined the results of thermal expansion.

2. Experimental

We used powdered samples of six pure wurtzite-type crystals BeO(5N), AlN(3N), GaN(4N), ZnO(5N), CdSe(5N) and CdS(5N). Diffraction peaks were measured at elevated temperatures under an argon or helium atmosphere using a heating stage in an X-ray diffractometer (RIGAKU RAD-200B) with Cu K_α radiation. Measurements were conducted up to 1373 K for BeO, AlN, and ZnO, however they were limited to 773 K for CdS, 973 K for CdSe and 1173 K for GaN due to sublimation of the samples at higher temperatures. The calibration of the diffraction angles was carried out by measuring the diffraction peaks from a standard silicon sample. Based on the angles of the diffraction peaks from the samples, the lattice parameters of the *a*- and *c*-axes were evaluated within a measurement error of 5×10^{-4} Å.

3. Results

Figs 1 and 2 show the temperature dependence of the lattice parameters *a* and *c*, respectively, for six wurtzite-type crystals. Generally, both the *a* and *c* values change nonlinearly with temperature; the thermal expansion coefficient defined by $\alpha_\perp = (1/a)(\mathrm{d}a/\mathrm{d}T)$ or $\alpha_\parallel = (1/c)(\mathrm{d}c/\mathrm{d}T)$ increases with increasing temperature. Suffixes $\perp$ and $\parallel$ denote the directions perpendicular and parallel to the *c*-axis, respectively. The lattice parameters of each crystal can be fitted by a quadratic function of temperature, i.e., *a* or $c = p + qT + rT^2$, in the measured temperature range. The fitted relation for each crystal is shown in the figures.

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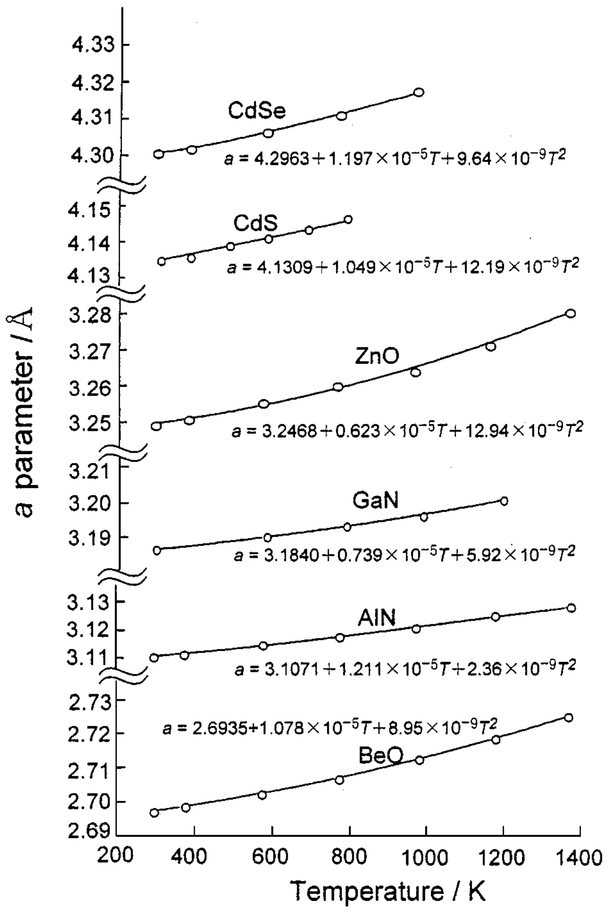

Figure 1 Temperature dependence of the lattice parameters a of six wurtzite-type crystals. Fitted equations are given in the figure.

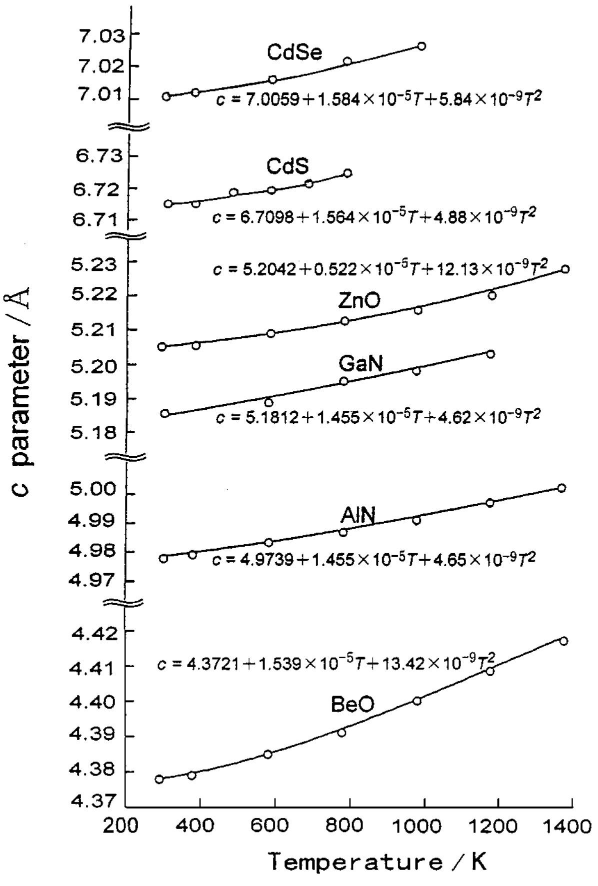

Figure 2 Temperature dependence of the lattice parameters c of six wurtzite-type crystals. Fitted equations are given in the figure.

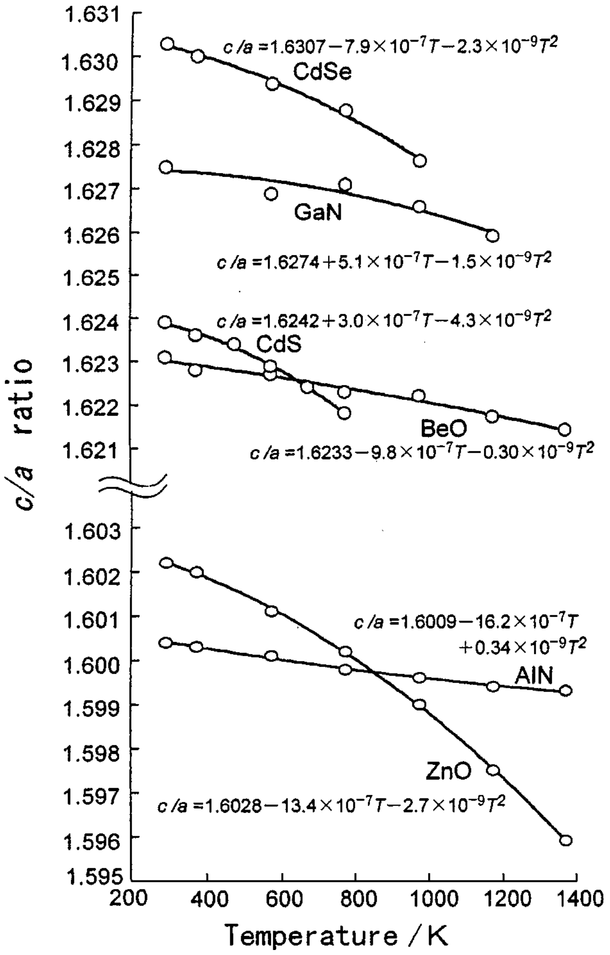

Figure 3 Temperature dependence of the c/a ratios of six wurtzite-type crystals. Fitted equations are given in the figure.

In Fig. 3, the temperature dependence of the c/a ratio for each crystal is plotted. The c/a ratio decreases with increasing temperature in all crystals. The fitted quadratic functions of temperature are shown in the figure.

4. Discussion

Thermal expansion measurements have previously been compiled for BeO, AlN, ZnO, CdSe and CdS in a data file [1]. The present results are consistent with the previous data except for the c parameter of ZnO; the previous results revealed that the temperature dependence of the c parameter in ZnO has an inflection point at approximately 800 K with an anomalous decrease of the thermal expansion coefficient at higher temperatures, while in the present results, no anomaly was observed.

Table I lists the lattice parameters and their ratios at 300 K, the thermal expansion coefficients α at 300 K, and the average thermal expansion coefficient between 300 K and 900 K α'. The thermal expansion coefficients of the wurtzite-type crystals range from 2.5 to 8 times 10^{-6}/K. These values are one order of magnitude smaller than those of metallic crystals and are of the same order as covalent crystals like Ge and Si.

It should be noted that in every wurtzite-type crystal, $\alpha_{\parallel}$ is smaller than $\alpha_{\perp}$, resulting in a decrease of

TABLE I The lattice parameters and their ratios, the thermal expansion coefficients at 300 K $\alpha_\perp$ and $\alpha_\parallel$, their average values between 300 K and 900 K $\alpha'_\perp$ and $\alpha'_\parallel$, and the calculated Grüneisen parameters in the directions perpendicular and parallel to the c-axis and their ratios

	BeO	AlN	GaN	ZnO	CdSe	CdS
$a_{300\text{K}}$ (Å)	2.6975	3.1111	3.1868	3.2495	4.3007	4.1363
$c_{300\text{K}}$ (Å)	4.3781	4.9788	5.1863	5.2064	7.0113	6.7154
c/a	1.623	1.600	1.627	1.602	1.630	1.624
$\alpha_\perp$ (10^{-6} K^{-1})	5.99	4.35	3.43	4.31	4.13	4.30
$\alpha_\parallel$ (10^{-6} K^{-1})	5.35	3.48	3.34	2.49	2.76	2.77
$\alpha_\perp/\alpha_\parallel$	1.12	1.25	1.03	1.73	1.50	1.55
$\alpha'_\perp$ (10^{-6} K^{-1})	7.96	4.79	4.69	6.70	5.47	6.06
$\alpha'_\parallel$ (10^{-6} K^{-1})	7.18	4.04	3.87	3.98	3.26	3.20
$\alpha'_\perp/\alpha'_\parallel$	1.11	1.19	1.21	1.68	1.68	1.74
$\gamma_\perp$ (300 K)	1.45	1.15	0.87	0.60	0.27	0.43
$\gamma_\parallel$ (300 K)	1.32	0.92	0.87	0.51	0.27	0.40
$\gamma_\perp/\gamma_\parallel$	1.10	1.26	1.01	1.18	1.00	1.08

the c/a ratio with increasing temperature. It has been shown that the stacking fault energies of wurtzite crystals are an increasing function of the c/a ratio, indicating that the smaller the c/a ratio, the more stable is the wurtzite-type structure with respect to the zincblende structure [2, 3]. Thus, the present results indicate that the wurtzite structure becomes more stable as the temperature is increased.

$\alpha'_\perp$–$\alpha'_\parallel$ is approximately 3×10^{-6}/K for ZnO and 2×10^{-6} K for CdSe and CdS. As a result, when a polycrystalline aggregate annealed at 800 K is cooled to 300 K, an internal stress of (1–1.5) $\times 10^{-3}$ times the elastic modulus can be produced at a boundary between grains having orthogonal orientations. The internal stress can be as large as 300 MPa for ZnO and 80 MPa for CdSe and CdS. These values are far higher than the yield stresses of these crystals at room temperature [4] and hence, plastic zones must appear at the boundary region.

Various physical parameters of each crystal, density d, elastic stiffness constants c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, bulk modulus K [5–7], specific heat at constant pressure at 300 K C_p [8], Phillips' ionicity f_i and effective charge e^* [9] are listed in Table II. The anisotropy of the thermal expansion is large in CdSe, CdS and ZnO but not in BeO, AlN and GaN. We note that the ionicities of the first three crystals are higher than those of the latter three, suggesting a role of the ionicity in the anisotropic thermal expansion.

The thermal expansion reflects the anharmonicity of the potential of crystal binding. The volume expansion coefficient α_v is correlated with the specific heat at constant volume C_v as

$$\alpha_\text{v} = \gamma \frac{\kappa C_\text{v}}{3V} \tag{1}$$

where κ is the compressibility (reciprocal of the bulk modulus), V is the volume, and the nondimensional coefficient γ is the Grüneisen parameter. The Grüneisen parameter represents the degree of anharmonicity of the crystal lattice and is expressed by the Debye model as

$$\gamma = -\frac{d \ln \theta_\text{D}}{d \ln V}, \tag{2}$$

where θ_D is the Debye temperature. In crystalline solids, the specific heat at constant volume C_v can be well approximated by the specific heat at constant pressure C_p within an accuracy of a few percent. For crystals with an axial symmetry such as the hexagonal wurtzite-type crystals, the Grüneisen parameter $\gamma_\parallel$ along the symmetry axis and $\gamma_\perp$ in the direction perpendicular to it can be separately expressed as [10]

$$\gamma_\perp = \frac{V}{C_\text{v}}\{(c_{11} + c_{12})\alpha_\perp + c_{13}\alpha_\parallel\}$$
$$\gamma_\parallel = \frac{V}{C_\text{v}}(2c_{13}\alpha_\perp + c_{33}\alpha_\parallel), \tag{3}$$

where c_{ij} are the elastic stiffness constants. Using the values listed in Table II, the Grüneisen parameters γ at 300 K have been calculated. The results are presented in Table I. The γ values of the wurtzite-type crystals

TABLE II Various material parameters of six wurtzite-type crystals: elastic compliances, bulk modulus K [5–7], density d, specific heat at constant pressure C_p [8], Phillips' ionicity f_i, and effective charge e^* [9]

	BeO	AlN	GaN	ZnO	CdSe	CdS
c_{11} (GPa)	470	411	296	210	74.9	84.3
c_{12} (GPa)	168	149	130	121	46.1	52.1
c_{13} (GPa)	119	99	158	105	39.3	46.4
c_{33} (GPa)	494	389	267	211	84.5	93.8
c_{44} (GPa)	153	125	24	42	13.2	15.0
K (GPa)	224	211	195	144	53.7	60.8
$d(g \cdot \text{cm}^{-3})$	3.01	3.26	4.60	5.68	5.81	4.82
C_p (300 K) (cal $\cdot$ g^{-1} K^{-1})	0.244	0.177	0.118	0.118	0.086	0.082
f_i	0.602	0.449	0.500	0.616	0.699	0.685
e^* (e)	0.61	0.47	—	0.53	0.41	0.41

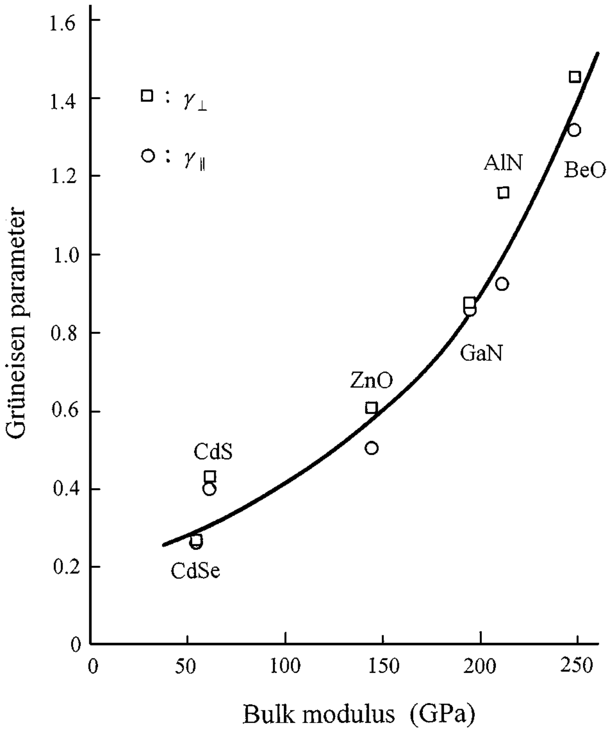

Figure 4 Relation between the Grüneisen parameter and the bulk modulus.

vary largely among crystals, ranging between 0.27 and 1.45. The γ values have a positive correlation with the bulk modulus, as shown in Fig. 4; the harder the crystal, the larger the Grüneisen parameter. Due to this correlation, thermal expansion coefficients do not differ among crystals as much as the Grüneisen parameters. The Grüneisen parameters in wurtzite-type crystals are smaller than those of metallic crystals ($\gamma = 1.5$–2.5) and ionic crystals ($\gamma \fallingdotseq 1.5$), and resemble the values of covalent crystals like Si ($\gamma = 0.50$ at 300 K) and Ge ($\gamma = 0.75$ at 300 K). In BeO, AlN and GaN, the anisotropy of the thermal expansion corresponds to the anisotropy of the Grüneisen parameter, $\gamma_\perp/\gamma_\parallel$, but in ZnO, CdSe and CdS, the anisotropy of the thermal expansion is considerably larger than the anisotropy of Grüneisen parameter. This suggests that the large anisotropic thermal expansion in the latter three crystals is not due to the anisotropic anharmonicity but is a result of the elastic anisotropy. The anisotropy of the Grüneisen parameters is well correlated with the c/a ratios of the crystals, as shown in Fig. 5, indicating that the anisotropy of the anharmonicity is related to the distortion of the tetrahedral bonding. Thus, the anisotropic thermal expansion in wurtzite-type crystals is associated with the anisotropies of both elasticity and anharmonicity.

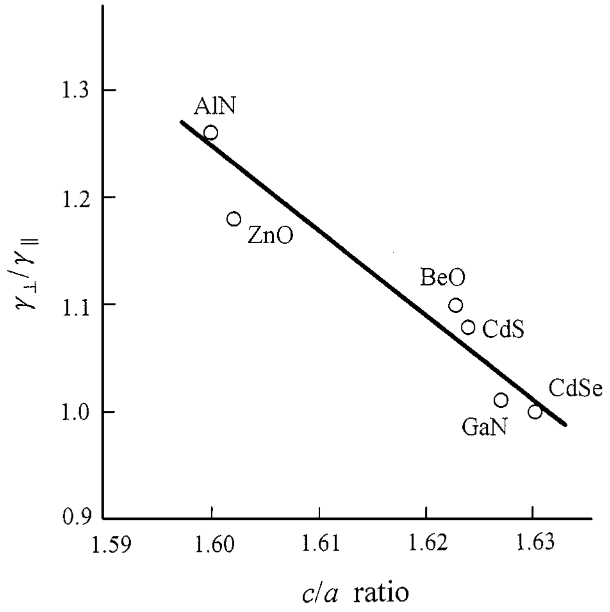

Figure 5 Relation between anharmonicity anisotropy, $\gamma_\parallel/\gamma_\perp$, and the c/a ratio.

5. Summary

The temperature dependence of the lattice parameters of six wurtzite-type crystals, BeO, AlN, GaN, ZnO, CdSe, and CdS, was measured by X-ray powder diffractometry. The thermal expansion coefficient generally increases with increasing temperature. The thrmal expansion along the a-axis is larger than that along the c-axis, resulting in a decrease of the c/a ratio with increasing temperature. The anisotropy in the thermal expansion is more than 50% in ZnO, CdS and CdSe. The calculated Grüneisen parameters range between 0.27 and 1.45 and have a positive correlation with the bulk moduli. The anisotropic thermal expansion is found to be associated with the anisotropies of both elasticity and anharmonicity.

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