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Low-temperature thermal expansion of spinel

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Abstract. The lattice parameter of synthetic spinel, MgAl_2O_4 , has been determined over the temperature range 77-300 K. The results can be expressed in the form

$$a = 8.0739 + 3.565 \times 10^{-8} T^2 + 9.90 \times 10^{-11} T^3$$

where a is the lattice parameter in Å at T K, and are consistent with measurements previously reported for ranges of temperature above room temperature. The corresponding variation for the linear coefficient of thermal expansion is derived. This shows that spinel has a thermal expansion only slightly greater than that of silicon and of the III-V semiconductors for which materials it has been used as an epitaxial substrate.

1. Introduction

Measurements of the lattice parameters of natural and synthetic spinel have been published for several ranges of high temperature down to room temperature (Henderson and Taylor 1975, Singh *et al* 1975, Suzuki and Kumazawa 1980) but we believe that this is the first report of work over a low-temperature range. The earlier results showed that spinel possesses a rather low coefficient of thermal expansion at room temperature and this feature together with the close relationship of its crystal structure to that of diamond (Bragg 1915, Grimes *et al* 1983) suggested that a lower-temperature investigation might be worthwhile. As is well known, spinel is an excellent substrate for the epitaxial growth of silicon, which crystallizes with diamond structure, and the related III-V semiconductors (Manasevit and Forbes 1966, Wang *et al* 1974). Further interest arises from the fact that these semiconductors are among the special class of cubic materials which exhibit a negative coefficient of thermal expansion at low temperature (Gibbons 1958, Carr *et al* 1965, Smith and White 1975, Lyon *et al* 1977).

2. Experimental details

The polycrystalline sample of MgAl_2O_4 used in this investigation was produced from equimolar proportions of high-purity MgO and Al_2O_3 . These constituents were thoroughly mixed and then subjected to several stages of hydraulic pressure followed by firing in oxygen, the sample being re-ground and re-pressed between consecutive firings. The final stage involved firing at 1700 K for 24 h. The resulting white compound

gave an extremely clean polycrystalline x-ray diffraction pattern with no evidence of the parent oxides or other impurity phases.

The lattice parameter of this prepared material was measured by the x-ray powder diffraction method using a Philips diffractometer fitted with step-scanning facilities and an Oxford Instruments continuous-flow low-temperature cryostat. The latter possessed a calibrated linear temperature sensor and provided control to ± 0.5 K over most of the investigated temperature range. An internal calibration standard was also incorporated by mixing the spinel powder with pure silicon in the ratio 7:3. Silicon is an ideal reference as its diffraction pattern has relatively few lines that fall conveniently close to, but clearly separate from, the important lines of the spinel pattern. A high-precision study of expansivity and lattice parameter variation in silicon has been published by Batchelder and Simmons (1964).

We used the centroid as a measure of diffraction-line position because of its advantages for the correction of aberrations (Wilson 1963) and the two diffraction lines (751) and (931) to determine the spinel cell parameter. With Cu $K\alpha$ radiation (for which we have used the weighted mean of $K\alpha_1$ and $K\alpha_2$ as the centroid wavelength, i.e. 1.54184 Å) these lines occur at a conveniently high angle and have the two strong silicon lines (531) and (620) as useful companions. The experimental procedure was thus to step-scan each of these four diffraction lines at each chosen temperature within the range 77–300 K at temperature intervals of approximately 10 K. The lattice parameter result finally taken at each temperature, for the prepared spinel sample, was achieved by averaging the values obtained from the corrected centroid positions of the (751) and (931) diffraction lines.

3. Results

The final results for the lattice parameter of spinel at the investigated temperatures are summarized in table 1. If these are fitted to a polynomial in absolute temperature T using a least squares procedure it is found that they can be represented to within two standard deviations of the experimental error by the expression

$$a = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \quad (1)$$

where $a_0 = 8.0739(2) \pm 0.0001$ Å; $a_1 \sim 0.0$; $a_2 = 3.565 \pm 0.005 \times 10^{-8}$ Å K⁻² and $a_3 = 9.90 \pm 0.01 \times 10^{-11}$ Å K⁻³. It is worth noting that the coefficient of the linear term was found to be negligible. This was not anticipated, but it is consistent with the third law of thermodynamics which demands that $\alpha \rightarrow 0$ as $T \rightarrow 0$ K.

If the linear coefficient of thermal expansion is now defined by $\alpha = \Delta a/a_R \Delta T$, where the reference lattice parameter a_R is taken to be that at 293 K, then the corresponding expression for α is given by

$$\alpha = 8.825 \times 10^{-9} T + 3.67 \times 10^{-11} T^2 \quad (2)$$

Thus, values for the linear coefficient of thermal expansion could be calculated for any chosen temperature within the range investigated; some results thus obtained are shown in table 2.

Finally, as measured values for isothermal bulk modulus $B_T = 1.95$ Mbar (Lewis 1966), molar volume, V , and heat capacity over a range of temperatures (King

Table 1. Lattice parameter results for MgAl_2O_4 .

T (K)	$a_{\text{cor}}(751)$ (Å)	$a_{\text{cor}}(931)$ (Å)	a_{exptl} (Å)	a_{polynom} (Å)
77.5	8.07465	8.07405	8.07435	8.07419
89.6	8.07441	8.07377	8.07409	8.07429
99.6	8.07481	8.07413	8.07447	8.07438
110.3	8.07473	8.07443	8.07458	8.07450
120.0	8.07473	8.07433	8.07453	8.07462
130.0	8.07482	8.07452	8.07467	8.07475
140.0	8.07498	8.07470	8.07484	8.07490
150.0	8.07586	8.07462	8.07524	8.07507
160.0	8.07525	8.07518	8.07522	8.07525
171.1	8.07560	8.07530	8.07545	8.07547
180.9	8.07577	8.07567	8.07572	8.07569
189.8	8.07595	8.07595	8.07595	8.07590
199.8	8.07586	8.07614	8.07600	8.07615
210.3	8.07654	8.07624	8.07639	8.07644
220.1	8.07698	8.07680	8.07689	8.07672
230.3	8.07690	8.07719	8.07705	8.07704
240.0	8.07759	8.07729	8.07744	8.07736
250.0	8.07759	8.07805	8.07782	8.07772
259.6	8.07829	8.07767	8.07798	8.07808
270.1	8.07829	8.07863	8.07846	8.07850
300.1	8.08043	8.07967	8.07989	8.07984

Table 2. Calculated values for the linear coefficient of thermal expansion and Gruneisen parameter.

T (K)	Molar volume cm^3	Linear coefficient of thermal expansion (10^6 K^{-1})	Gruneisen parameter, γ
77.5	39.623	0.90	1.69
89.6	39.624	1.09	1.44
99.6	39.626	1.24	1.30
110.3	39.628	1.42	1.18
120.0	39.629	1.59	1.11
130.0	39.631	1.77	1.06
140.0	39.633	1.95	1.01
150.0	39.636	2.15	0.99
160.0	39.639	2.35	0.98
171.1	39.642	2.58	0.96
180.9	39.645	2.80	0.96
189.8	39.648	3.00	0.97
199.8	39.652	3.23	0.97
210.3	39.656	3.48	0.98
220.1	39.660	3.72	1.00
230.3	39.665	3.98	1.02
240.0	39.670	4.23	1.04
250.0	39.675	4.50	1.06
259.6	39.680	4.76	1.08
270.1	39.687	5.06	1.12
300.1	39.706	5.95	1.21

1955) are already available for spinel (see also Grimes 1972), we have calculated the Gruneisen parameter

$$\gamma = 3\alpha B_T V / C_V \quad (3)$$

for the temperatures quoted in table 2. This shows that α lies in the range 1.0–1.2 from 100–300 K but appears to rise above these values below 100 K. The latter is explained partly as a consequence of an increase in bulk modulus (B_T is about 7.5% larger at 4.2 K according to Pointon and Taylor 1968) but may also reflect an increasing departure from harmonic behaviour (low-temperature anharmonicity is well known among spinel compounds—see, for example, Grimes 1974, Dawes *et al* 1974) and/or an increasing systematic error in the determination of α with decreasing temperature. The experimental uncertainty associated with α could rise to $\pm 50\%$ at the lowest temperature investigated here.

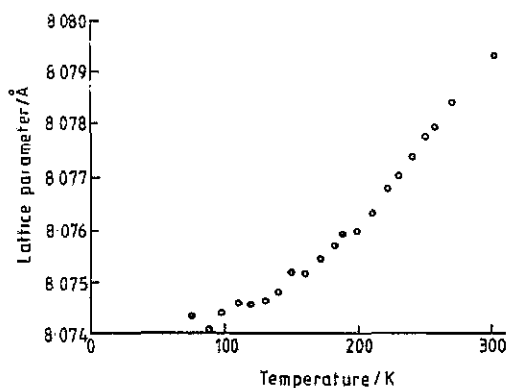


Figure 1. Averaged values for the lattice parameter of MgAl_2O_4 spinel as a function of temperature.

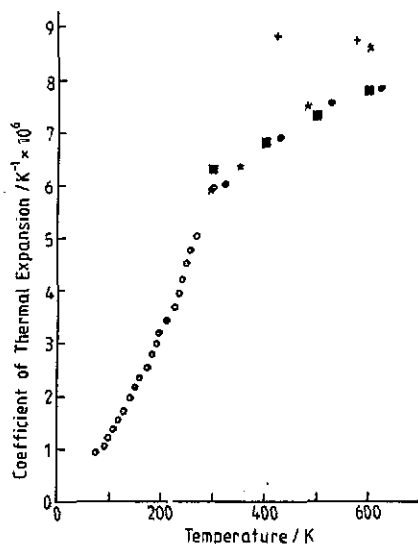


Figure 2. Coefficient of thermal expansion of MgAl_2O_4 spinel as a function of temperature—comparison with previously published results: \circ , present; +, Beals and Cook (1957); \blacksquare , Henderson and Taylor (1975); *, Singh *et al* (1975); \bullet , Suzuki and Kumazawa (1980). Note that according to the last reference, there exists a λ anomaly at 923 K, whose tail may make a significant contribution above 700 K.

4. Discussion

The unit-cell parameter of spinel is known to be a sensitive function of stoichiometry (Jagodzinski and Saalfeld 1957), with polycrystalline material produced by ceramic

techniques being typically non-stoichiometric, i.e. having a lattice parameter significantly lower than a good stoichiometry single crystal. Nevertheless, the results for the coefficient of thermal expansion derived here from the observed variation of lattice parameter with temperature are probably reasonably characteristic of spinel. Certainly, our results are consistent with those obtained at higher temperatures by previous workers including Suzuki and Kumazawa (1980) whose experiment related to a single crystal. This is shown in figure 2.

As before, the experimental values for α tend to be low, but, though α decreases further with decreasing temperature, following the molar heat capacity as suggested by Gruneisen's law, there is no indication that the coefficient of thermal expansion might go negative despite the close crystal-structure relationship of spinel with silicon and the III-V semiconductors. Indeed, as a negligible coefficient has been found for the linear term in the expression for the lattice parameter, (1), and the coefficients of T^2 and T^3 are positive in this polynomial, it seems that spinel could exhibit a classical smooth behaviour right down to absolute-zero temperature. Conversely, if there is a region of negative expansion, it is likely to occur in the 0–4 K temperature range and careful experimental measurements will be required if it is to be revealed.

In the absence of such data, it would appear that spinel may be untypical of its isomorphs, for negative coefficients of thermal expansion have been observed among these compounds—see, for example, CdCr_2S_4 (Martin *et al* 1969). However, the sulphide and selenide spinels are also semiconducting, like silicon, and it may be that this additional feature of similarity (which may be indicative of the presence of some covalency, i.e., non-central forces) is actually needed to create the conditions leading to a negative coefficient of thermal expansion in the low-temperature regime (Gilat 1977).

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