THERMO-OPTIC BEHAVIOUR OF SILICON CARBIDE

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1. INTRODUCTION

SILICON CARBIDE (carborundum) is a trigonal crystal which crystallises in thin basal plates. It is colourless when pure, but usually coloured green, blue, or black due to impurities of small amounts of iron, alumina, carbon, etc. It is uniaxial positive with extremely high refraction, strong birefringence and very strong dispersion. The refractive indices of carborundum, both ordinary and extraordinary, has been determined by Weigel (1915) and by Merwin (1917) for the visible region. Weigel has also determined the rate of variation of the ordinary as well as the extraordinary refractive index with temperature over three ranges of temperature and for four wavelengths. In this paper it is proposed to discuss the thermo-optic behaviour of carborundum, utilising Weigel's data and applying the theory of thermo-optic behaviour of solids due to Dr. G. N. Ramachandran (1947).

2. DERIVATION OF THE DISPERSION FOURMULÆ

The derivation of accurate dispersion formulæ is a necessary step to the theoretical explanation of the thermo-optic behaviour of solids. As the data available cover a limited range, a dispersion formula involving the fewest absorption wave-lengths would seem the most appropriate. In fact, an attempt was made to derive a dispersion formula using only one absorption wave-length of the following type:

$$n_i{}^2 = 1 + \frac{k\lambda^2}{\lambda^2 - \lambda_1{}^2}, \; n_i = \omega, \; \epsilon.$$

This was found to fail, as the same dispersion wave-length did not satisfy the formulæ for the ordinary and the extraordinary refractive indices. In other words, a mere change in the oscillator strength is incapable of explaining the birefringence of carborundum with this type of formula. An attempt was therefore made to fit in the data using two frequencies in the dispersion formula, *viz.*, by formulæ of the following type:

$$\omega^2 = 1 + \frac{k_1\lambda^2}{\lambda^2 - \lambda_1{}^2} + \frac{k_2\lambda^2}{\lambda^2 - \lambda_2{}^2} \tag{1}$$

$$\epsilon^2 = 1 + \frac{k_3\lambda^2}{\lambda^2 - \lambda_1{}^2} + \frac{k_4\lambda^2}{\lambda^2 - \lambda_2{}^2}. \tag{2}$$

The constants are found to be:

$$k_1 = 3\cdot657, \quad k_2 = 1\cdot898,$$
$$k_3 = 1\cdot626, \quad k_4 = 4\cdot110,$$
$$\lambda_1 = 155 \ m\mu, \quad \lambda_2 = 175 \ m\mu.$$

(The wave-lengths are measured in millimicrons.)

In Table I, the calculated and experimental values are compared and the formulæ are seen to agree very well. The agreement of the dispersion formulæ with experimental values justifies the assumption that the dispersion frequencies are the same for the ordinary and the extraordinary indices but that only their strengths alter with the direction of the electric vector.

TABLE I

ω = Ordinary refractive index

λ	ω (obs.)	ω (cal.)	Difference
436	2·7292	2·7292	0·0000
455	2·7138	2·7138	0·0000
492	2·6894	2·6894	0·0000
502	2·6842	2·6838	−0·0004
546	2·6632	2·6632	0·0000
578	2·6513	2·6514	+0·0001
588	2·6481	2·6481	0·0000
668	2·6271	2·6273	+0·0002
706	2·6195	2·6195	0·0000

TABLE II

ϵ = Extraordinary refractive index

λ in $m\mu$	ϵ (obs.)	ϵ (cal.)	Difference
436	2·7859	2·7859	0·0000
455	2·7677	2·7682	+0·0005
492	2·7401	2·7405	+0·0004
502	2·7342	2·7342	0·0000
546	2·7106	2·7109	+0·0003
578	2·6974	2·6974	0·0000
588	2·6939	2·6939	0·0000
668	2·6707	2·6705	−0·0002
706	2·6623	2·6623	0·0000

3. THERMAL VARIATION OF THE REFRACTIVE INDICES

We now apply Ramachandran's theory of thermo-optic behaviour to this case. The theory considers the variation of refractive index with temperature as due to the sum of two effects, one arising from a change of

volume which causes a change in the number of dispersion centres, and the other from a shift in the position of the dispersion wave-lengths. So, differentiating (1) and (2) with respect to temperature t, we get

$$\frac{d\omega}{dt} = -\frac{\gamma}{2\omega}(\omega^2 - 1) + \frac{1}{\omega}\frac{k_1\lambda^4}{(\lambda^2 - \lambda_1^2)^2}\chi_1 + \frac{1}{\omega}\frac{k_2\lambda^4}{(\lambda^2 - \lambda_2^2)^2}\chi_2 \qquad (3)$$

$$\frac{d\epsilon}{dt} = -\frac{\gamma}{2\epsilon}(\epsilon^2 - 1) + \frac{1}{\epsilon}\cdot\frac{k_3\lambda^4}{(\lambda^2 - \lambda_1^2)^2}\chi_1 + \frac{1}{\epsilon}\frac{k_4\lambda^4}{(\lambda^2 - \lambda_2^2)^2}\chi_2, \qquad (4)$$

where $\gamma =$ coefficient of cubical expansion.

$$\chi_1 = \frac{1}{\lambda_1}\left(\frac{d\lambda_1}{dt}\right), \quad \chi_2 = \frac{1}{\lambda_2}\left(\frac{d\lambda_2}{dt}\right).$$

Weigel has determined the temperature variation of the ordinary index for four wave-lengths and three temperature ranges, and the temperature variation of the extraordinary index for two wave-lengths and two temperature ranges. It is found that on making $\chi_1 = \chi_2 = \chi$, the value of χ satisfies the expressions for the variation with temperature of both the ordinary and the extraordinary refractive indices. The value of χ for the temperature range 20°–460° is found to be 35×10^{-6}. The values of χ and the corresponding $\frac{d\omega}{dt}$ and $\frac{d\epsilon}{dt}$ for different temperature ranges are given in Table III along with the experimental values.

TABLE III

Wave-length in $m\mu$	Temp. 20° — 460° C. $\gamma = 18 \times 10^{-6}$ $\chi = 35 \times 10^{-6}$		Temp. 460° — 760° C. $\gamma = 15 \times 10^{-6}$ $\chi = 42 \times 10^{-6}$		Temp. 760° — 1150° C. $\gamma = 13\cdot5 \times 10^{-6}$ $\chi = 45 \times 10^{-6}$	
	$\frac{d\omega}{dt} \times 10^5$ calc.	$\frac{d\omega}{dt} \times 10^5$ obs.	$\frac{d\omega}{dt} \times 10^5$ calc.	$\frac{d\omega}{dt} \times 10^5$ obs.	$\frac{d\omega}{dt} \times 10^5$ calc.	$\frac{d\omega}{dt} \times 10^5$ obs.
471	7·2	7·5	9·5	10·0		
554	6·6	6·6	8·6	8·2	9·7	9·7$_3$
650	6·4	6·1	8·4	7·6	9·3	9·0$_0$
668	6·3	6·9	8·1	7·4		
	$\frac{d\epsilon}{dt} \times 10^5$ calc.	$\frac{d\epsilon}{dt} \times 10^4$ obs.	$\frac{d\epsilon}{dt} \times 10^5$ calc.	$\frac{d\epsilon}{dt} \times 10^5$ obs.		
471	7·5	8·2	10	11·5		
668	6·5	6·3	8·5	8·0		

Table III shows that the theory explains the increase with temperature of both the ordinary and the extraordinary indices. It is seen also that the value of χ increases with temperature. Though the theory gives a decreasing $\dfrac{d\omega}{dt}$ and $\dfrac{d\epsilon}{dt}$ for increasing wave-lengths, this decrease is not quite so rapid as that appearing in the experimental data. The explanation of this discrepancy will be discussed presently.

4. COMPARISON WITH THE CASE OF DIAMOND

It is instructive to compare the behaviour of carborundum and diamond. Both substances have similar high refractivities, high dispersion and great hardness, while their structures exhibit a very similar disposition of the valence bonds. The compressibilities of diamond and carborundum are also not very different. The thermal expansion coefficient of carborundum is, however, six times greater than that for diamond, a circumstance which

TABLE IV

	Refractive index n_D	Hardness on Moh's Scale	Compressibility	Thermal expansion	χ	Principal Infra-red absorption
Diamond ..	2·42	10	$1 \cdot 6 \times 10^{-7}$ per atm.	3×10^{-6}	$7 \cdot 6 \times 10^{-6}$	8μ
Carborumdum	$\omega = 2 \cdot 65$ $\epsilon = 2 \cdot 69$	9·5	$2 \cdot 2 \times 10^{-7}$ per atm.	18×10^{-6}	35×10^{-6}	12μ

is no doubt connected with the notable difference in the vibration frequencies of the respective crystal structures. It will be noticed that the value of χ for carborundum is nearly five times larger than for diamond.

A more detailed comparison brings out some further points of interest. The dispersion formula for diamond is given by Ramachandran as

$$n^2 = 1 + \frac{4 \cdot 337 \, \lambda^2}{\lambda^2 - 106^2} + \frac{0 \cdot 3309 \, \lambda^2}{\lambda^2 - 175^2}.$$

This may be compared with the formulæ in the case of carborundum given above, *viz.*,

$$\omega^2 = 1 + \frac{3 \cdot 657 \, \lambda^2}{\lambda^2 - 155^2} + \frac{1 \cdot 898 \, \lambda^2}{\lambda^2 - 175^2}$$

$$\epsilon^2 = 1 + \frac{1 \cdot 626 \, \lambda^2}{\lambda^2 - 155^2} + \frac{4 \cdot 11 \, \lambda^2}{\lambda^2 - 175^2}.$$

The dispersion data in the case of diamond very clearly indicate a weak electronic absorption wave-length at $175 \, m\mu$. The electronic absorptions at $155 \, m\mu$ and $175 \, m\mu$ in carborundum evidently correspond to the strong

term at 106 $m\mu$ in diamond, the doubling being presumably connected with the anisotropy of structure of the former. Though the available data do not indicate any term or terms for carborundum corresponding to the absorption wave-length at 175 $m\mu$ in diamond, one may reasonably surmise the existence of a term or perhaps two such terms between 200 $m\mu$ to 250 $m\mu$. Such terms would not make a large contribution to the refraction or dispersion, but might nevertheless sensibly influence the temperature coefficient of the refractive indices in the direction of making it decrease more rapidly as the wave-length increases. It is suggested that this may be the origin of the discrepancies between the observed and calculated values appearing in Table III.

In conclusion, I wish sincerely to thank Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for his guidance and encouragement.

6. Summary

The dispersion and birefringence of carborundum are well represented by the formulæ

$$\omega^2 = 1 + \frac{k_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{k_2 \lambda^2}{\lambda^2 - \lambda_2^2}$$

$$\epsilon^2 = 1 + \frac{k_3 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{k_4 \lambda^2}{\lambda^2 - \lambda_2^2}, \text{ where}$$

$\lambda_1 = 155\ m\mu,\ \lambda_2 = 175\ m\mu,\ k_1 = 3\cdot657,\ k_2 = 1\cdot898,$
$k_3 = 1\cdot626,\ k_4 = 4\cdot11.$

The theory of thermo-optic behaviour of solids when applied to the case of carborundum explains the observed positive temperature coefficient of both the indices.

References

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