THE DISPERSION AND THERMO-OPTIC BEHAVIOUR OF VITREOUS SILICA

By S. Chandrasekhar

(*From the Raman Research Institute, Bangalore*)

Received August 20, 1951
(Communicated by Sir C. V. Raman, N.L.)

1. Introduction

As is well known, vitreous silica is obtained by the fusion of crystalline quartz at a temperature abve 1700° C. and subsequent solidification. The chemical composition is unaltered by the process, but there is a considerable diminution in the density which falls from 2·651 to 2·203. Another noteworthy change is the diminution of the coefficient of thermal expansion at room temperatures which is 36×10^{-6} for quartz and only $1·5 \times 10^{-6}$ for vitreous silica.

The Raman spectrum of vitreous silica has been studied by several investigators (Gross and Romanova, 1929; Kujumzelis, 1935). It differs from that of crystalline quartz but nevertheless exhibits certain features in common with it. The change may be described by the statement that the sharp lines in the Raman spectrum of quartz become diffuse bands for the vitreous silica.

The infra-red absorption of vitreous silica has been examined upto $8\,\mu$ (Drummond, 1936). It follows closely the behaviour of quartz, except that the peaks of absorption are not so sharp and well defined.

Tousey (1940) has observed with crystalline quartz two sharp reflection maxima in the ultra-violet analogous to the Reststrahlen in the infra-red, at 1060 A.U. and 1190 A.U. respectively. For vitreous silica he observed two similar bands in almost the same positions to within 20 A.U. but less intense.

In this paper, it is proposed to consider the refractivity, dispersion and the thermo-optic behaviour of vitreous silica, taking into consideration the facts stated above.

2. The Refraction and Dispersion of Vitreous Silica

In view of the fact that quartz and vitreous silica are of the same chemical composition and since their spectroscopic behaviour is also closely similar, one expects that it should be possible to calculate the refractivity and

275

dispersion of vitreous silica from those of quartz by taking into account the disappearance of the optical anisotropy and the diminution of density occurring in its formation. One or another of three well-known formulæ connecting refractive index with density can be used to calculate the refractive index of vitreous silica, namely the Lorentz-Lorenz, the Drude and the Gladstone Dale respectively. In doing this, the index of quartz for each wavelength is obtained by adding twice the ordinary index to the extraordinary index and dividing by three. The observed indices of vitreous silica are given for comparison with the values thus calculated in Table I.

TABLE I

λ (in μ)	Mean n at 18° C. for quartz	n (expt.) at 18° C. for vitreous silica	Lorentz-Lorenz		Drude		Gladstone and Dale	
			n (calc.)	$n_{calc.} - n_{expt.}$	n (calc.)	$n_{calc.} - n_{expt.}$	n (calc.)	$n_{calc.} - n_{expt.}$
·193583	1·664470	1·55999	1·52900	−0·0310	1·57203	+0·0120	1·55218	−0·0078
·20255	1·649850	1·54727	1·51805	−0·0292	1·55910	+0·0118	1·54030	−0·0070
·250329	1·604010	1·50745	1·48344	−0·0240	1·51890	+0·0115	1·50193	−0·0055
·340365	1·570775	1·47867	1·45818	−0·0205	1·48928	+0·0106	1·47432	−0·0044
·434047	1·557110	1·46690	1·44772	−0·0192	1·47778	+0·0109	1·46296	−0·0039
·546072	1·549233	1·46013	1·44168	−0·0185	1·47089	+0·0108	1·45642	−0·0037
·656278	1·544909	1·45640	1·43837	−0·0180	1·46711	+0·0107	1·45282	−0·0036
·794763	1·541449	1·45340	1·43571	−0·0179	1·46408	+0·0107	1·44995	−0·0035
Δn	0·123021	0·10659	0·09329		0·10795		0·10223	

From the table we observe that the error in refractivity is greatest with the Lorentz-Lorenz formula, while the Gladstone and Dale formula gives the best numerical fit. This error varies appreciably with the wavelength for the two formulæ mentioned above, while with the Drude formula it is almost independent of wavelength. At the foot of the table, the change in index as we proceed from the greatest to the least wavelength, Δn, is given. It is seen that the Drude formula represents the dispersion of vitreous silica best. The Gladstone and Dale formula gives good values for the refractivity but not the dispersion, while the Lorentz-Lorenz formula represents neither well. It is, therefore, proposed to consider only the Drude type of formula in the present discussion.

Dispersion formulæ for crystalline quartz have been suggested by many authors in the past. We shall here consider only that put forward by T. Radhakrishnan (1951) in these *Proceedings* which has the following merits: firstly, it fits very well both the ordinary and extraordinary indices over a wide range of wave-lengths, and secondly, all the absorption wave-lengths used in the formula have an experimental justification, except the extreme

ultraviolet wave-length of $0 \cdot 06\,\mu$ which is a hypothetical one. The formulæ respectively for the ordinary and extraordinary indices are:—

$$n_\omega{}^2 - 1 = \frac{0 \cdot 663044\,\lambda^2}{\lambda^2 - (0 \cdot 0600)^2} + \frac{0 \cdot 517852\,\lambda^2}{\lambda^2 - (0 \cdot 1060)^2} + \frac{0 \cdot 175912\,\lambda^2}{\lambda^2 - (0 \cdot 1190)^2}$$

$$+ \frac{0 \cdot 565380\,\lambda^2}{\lambda^2 - (8 \cdot 844)^2} + \frac{1 \cdot 675299\,\lambda^2}{\lambda^2 - (20 \cdot 742)^2} \qquad (1)$$

$$n_\epsilon{}^2 - 1 = \frac{0 \cdot 665721\,\lambda^2}{\lambda^2 - (0 \cdot 0600)^2} + \frac{0 \cdot 503511\,\lambda^2}{\lambda^2 - (0 \cdot 1060)^2} + \frac{0 \cdot 214792\,\lambda^2}{\lambda^2 - (0 \cdot 1190)^2}$$

$$+ \frac{0 \cdot 539173\,\lambda^2}{\lambda^2 - (8 \cdot 792)^2} + \frac{1 \cdot 8076613\,\lambda^2}{\lambda^2 - (19 \cdot 70)^2} \qquad (2)$$

From what has already been pointed out, it is reasonable to expect a similar formula to hold good for vitreous silica. Since the last two terms in the formula are of very minor importance in the visible region of the spectrum, we may without sensible error take the infra-red frequencies for vitreous silica to be those which function in the ordinary index of quartz. When a weighted mean of the oscillator strengths of the corresponding terms for the ordinary and extraordinary indices is taken and reduced proportionately to the density, the constants in the numerators turn out to be $0 \cdot 5517$, $0 \cdot 4263$, $0 \cdot 1570$, $0 \cdot 46$ and $1 \cdot 43$ respectively. From Table I we know that such a calculation would not exactly fit the refractivity of vitreous silica. It is necessary, in fact, to alter the oscillator strengths very slightly. The dispersion of vitreous silica at $18°\,C.$ is found to be well represented by the formula.

$$n^2 - 1 = \frac{0 \cdot 5320\,\lambda^2}{\lambda^2 - (0 \cdot 0600)^2} + \frac{0 \cdot 4151\,\lambda^2}{\lambda^2 - (0 \cdot 1060)^2} + \frac{0 \cdot 1570\,\lambda^2}{\lambda^2 - (0 \cdot 1190)^2}$$

$$+ \frac{0 \cdot 4538\,\lambda^2}{\lambda^2 - (8 \cdot 844)^2} + \frac{1 \cdot 4460\,\lambda^2}{\lambda^2 - (20 \cdot 742)^2} \qquad (3)$$

The experimental values for the refractive indices (Sosman, 1927) are given with the calculated values in Table II.

TABLE II

λ (in μ)	n (experimental)	n (calculated)
·193583	1·55999	1·55995
·20255	1·54727	1·54732
·231288	1·51941	1·51950
·250329	1·50745	1·50747
·274867	1·49617	1·49624
·396848	1·47061	1·47054
·479991	1·46355	1·46355
·546072	1·46013	1·46012
·643847	1·45674	1·45673
·656278	1·45640	1·45642
·706520	1·45517	1·45517
·794763	1·45340	1·45343

As can be seen, the agreement between the calculated and experimental values is very satisfactory, thereby indicating that the behaviour of quartz and of vitreous silica in regard to refraction and dispersion are very similar to each other. No doubt, a slight change of oscillator strength has been found necessary in the formula, but this is not surprising considering the striking change of structure between these two forms of silica as is revealed by X-ray investigations.

3. THE VARIATION OF REFRACTIVE INDEX WITH TEMPERATURE

The refractive indices of vitreous silica increase notably with temperature. Indeed, the increase in index for a given wave-length over a range of $1000°$ C. is approximately of the same order as the change in index for a particular temperature as we proceed from the visible to the ultra-violet region. Also dn/dt itself varies with wavelength, increasing rapidly with increase of frequency. The thermal expansion of vitreous silica being extremely small, it can contribute very little to the change in refractive index, and even so it would reduce and not increase the index. Thus, considering the position in the light of the remarks already made regarding the dispersion formula of vitreous silica, the only explanation that could reasonably be put forward for the increase of the refractive indices with rise of temperature is that there is a fall in the characteristic absorption frequencies of the material in the ultra-violet region of the spectrum. This indeed is the idea put forward by G. N. Ramachandran (1947 *a*) in his theory of the thermo-optic behaviour of solids. According to him, the temperature variation of the refractivity is due to two causes which usually work in opposite directions, *viz.*, a diminution due to the thermal expansion of the solid and an increase due to the downward shift of the characteristic frequencies of the substance in the ultra-violet. The expression for dn/dt is given by

$$\frac{dn}{dt} = -\frac{r(n^2 - 1)}{2n} + \frac{1}{n}\sum_r \frac{a_r \lambda^4 \lambda_r^2}{(\lambda^2 - \lambda_r^2)^2} \chi_r \qquad (4)$$

where γ is the coefficient of cubical expansion and χ_r is defined as $\frac{1}{\lambda_r}\frac{d\lambda}{dt}$ where λ_r is the characteristic absorption wave-length. In the present treatment, we shall neglect the variations of the infra-red frequencies with temperature, as the contribution of those terms is extremely small. We shall also consider the absorption wave-length in the extreme ultra-violet to be unchanged with temperature. This is justified, as the ultra-violet term arises as a result of inner electronic transitions in the atoms of silicon and oxygen which may be taken to be influenced very little by temperature. Even if they are affected by temperature, the ultra-violet term being sensibly a constant, it would not suffer an appreciable change in value. We are, therefore,

left with two terms for which χ is not equal to zero, namely, the terms containing the wave-lengths 1060 A.U. and 1190 A.U.   As these are very close to each other, we shall take it that their χ's are the same.

Measurements of *dn/dt* have been made for vitreous silica at a mean temperature of 60° C. by Martens (1904) for a series of wavelengths from 1850 A.U. to 6000 A.U.   A theoretical evaluation of *dn/dt* over this range of wave-lengths has already been made by G. N. Ramachandran (1947 *b*). But as the dispersion formula used by him was not the same, it appeared worth while to recalculate the figures using equation (4).   In doing so, the value of χ has been taken as $2·5 \times 10^{-5}$ which is almost the same as that deduced from the data of Rinne (1914) in the temperature range between 18° C. and 130° C. as shown below.   The calculated values are represented by a continuous curve in Fig. 1, while the circles show the experimental data of Martens, and the triangles indicate the data of Tilton and Tool
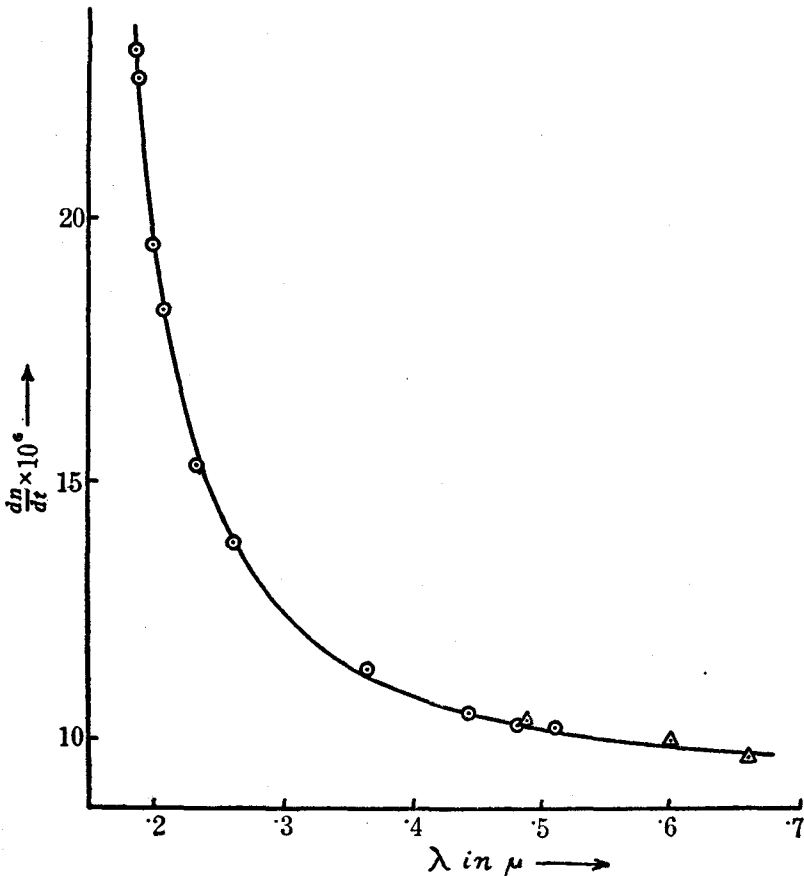

Fig. 1

(1929). It will be seen that the theoretical curve fits the data well over the entire range of wave-lengths.

4. The Shift of the Characteristic Frequencies with Temperature

The refraction of vitreous silica has been studied for a whole range of temperature from $-160°$ C. to $1000°$ C. for four wave-lengths in the visible region by Rinne (1944). The refractive index–temperature curves reveal that the index increases rapidly with temperature from $-160°$ to $475°$ C. Between $475°$ and $590°$ C. the rate of increase shows a drop which is exhibited as a flexure in all the curves about that region. Beyond $590°$ C., the curves again show a rapid rise. The course of the refractive index-temperature curve upto $500°$ C. has been discussed by Ramachandran (1947 b). The value of χ used by him in his calculations were obtained by comparison with the χ of the principal Raman line of α quartz, 465 cm.$^{-1}$, as determined by Nedungadi (1940) from $-180°$ to $500°$ C. In this work, it is proposed to actually determine χ at various temperatures from the values of dn/dt from Rinne's data (*loc. cit.*) from $-160°$ to $1000°$ C.

The method of evaluating χ will be described below. From eqn. (4) for dn/dt we notice that on substitution of dn/dt and γ, χ could be calculated. It is, however, important to realise, that, since the dispersion formula fits at $18°$ C., it is possible to evaluate χ from eqn. (4) only at that temperature. The same equation cannot be used to calculate χ at a higher temperature by a mere substitution of the values of dn/dt and γ at the higher temperature. This is because the coefficient of χ in eqn. (4) which is a function of λ_r, varies with temperature, or, in other words, the dispersion formula itself is, in reality, different for different temperatures. Therefore, in order to trace the approximate value of χ at various temperatures, the whole range is split up into small intervals. Using the value of χ at $18°$ C., λ_r is deter-

TABLE III

Range of temperature	$\chi \times 10^5$ $\lambda = \cdot 47135\,\mu$	$\chi \times 10^5$ $\lambda = \cdot 501568\mu$	$\chi \times 10^5$ $\lambda = \cdot 587563\,\mu$	$\chi \times 10^5$ $\lambda = \cdot 667815\,\mu$	Mean $\chi \times 10^5$
$-160°$ to $-64°$ C.	1·3	1·7	1·2	1·0	1·3
$-160°$ to $18°$ C.	1·8	1·6	1·5	1·4	1·6
$-64°$ to $130°$ C.	2·3	2·3	2·3	2·1	2·3
$18°$ to $130°$ C.	2·4	2·8	2·7	2·3	2·6
$18°$ to $235°$ C.	2·8	2·8	2·8	2·6	2·8
$130°$ to $365°$ C.	3·2	3·1	3·1	3·1	3·1
$235°$ to $475°$ C.	3·2	3·5	3·4	3·5	3·4
$365°$ to $590°$ C.	3·1	3·3	3·3	3·4	3·3
$475°$ to $590°$ C.	2·9	2·9	3·0	3·0	3·0
$475°$ to $1000°$ C.	··	3·7	3·6	3·7	3·7
$590°$ to $1000°$ C.	··	3·9	3·8	3·9	3·9

mined at the next higher range. By substituting for dn/dt and γ at this new range, the new value of χ may be calculated. Thus, by successively accounting for λ_r, χ has bean found from $-160°$ to $1000°$ C., and these values are given in Table III.
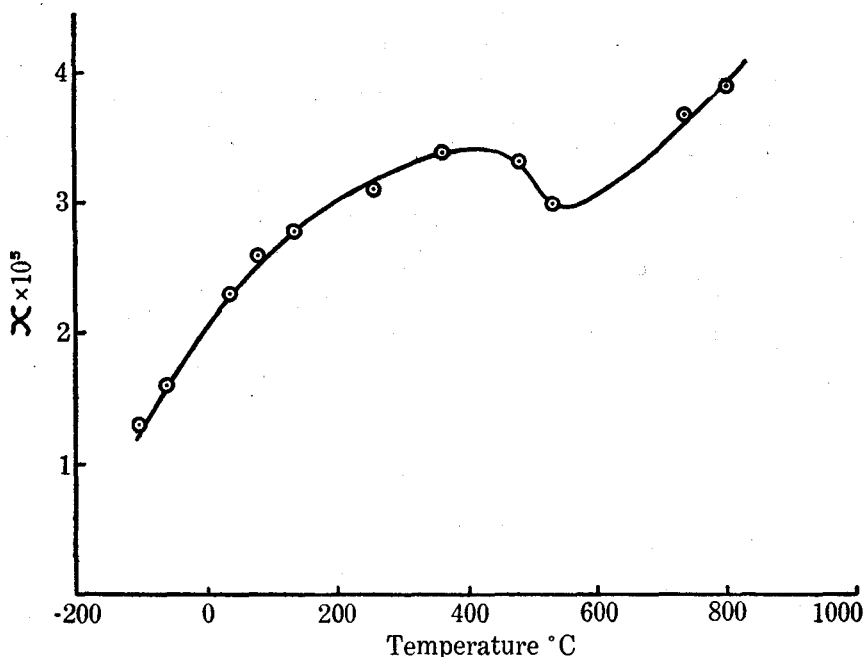

FIG. 2

From Table III we see that there are small differences in the value of χ in each line which are presumably due to the experimental errors in the data. As χ should be independent of the wave-length, its mean value has been given in the last column. A curve drawn connecting χ with temperature is shown in Fig. 2. It is seen that χ first increases with temperature and reaches a maximum at about $400°$ C., after which it drops, reaching a minimum value at about $560°$ C. beyond which it again rises rather steeply. The minimum of χ occurs, as nearly as can be judged with the present data, very close to the temperature of transition of quartz from the α to the β form. Various other physical properties of crystalline quartz exhibit noteworthy changes in the temperature range between $400°$. and the transition point. It is remarkable that this behaviour characteristic of crystalline quartz manifests itself even in the vitreous modification.

SUMMARY

The refractivity and the dispersion of vitreous silica are shown to be calculable from those of quartz by considering the diminished density. The temperature variation of its refractive indices over the entire range of wavelengths is in quantitative accord with the hypothesis that the characteristic absorption frequencies in the ultra-violet fall with rise of temperature. The rate of change of these frequencies has been traced from $-160°$ to $1000°$ C. and shows remarkable variations in the vicinity of the temperature at which the α-β transformation in crystalline quartz occurs.

REFERENCES

Gross and Romanova	..	*Zeits. f. Phys.*, 1929, **55**, 744.
Kujumzelis	..	*Ibid.*, 1935, **97**, 561; 100, 221.
Martens	..	*Ibid.*, 1904, **6**, 308.
Drummond	..	*Proc. Roy. Soc.*, 1936, **153**, 378.
Tousey	..	*Phys. Rev.*, 1940, **57**, 1060.
Radhakrishnan, T.	..	*Proc. Ind. Acad. Sc.*, 1951, **33**, 22.
Ramachandran, G. N.	..	*Ibid.*, 1947, **25** *a*, 266.
——————	..	*Ibid.*, 1947, **25** *b*, 280.
Nedungadi	..	*Ibid.*, 1940, **11**, 86.
Sosman	..	The Properties of Silica, 1927.
Rinne	..	*Neues. Jahrb. Min.*, 1914, **39**, 338.
Tilton and Tool	..	*Jour. Res. Bur. Stand.*, 1929, **3**, 619.