Molar refraction of quartz family minerals

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Abstract. Different polymorphs of silica and the opals exhibit significant variations in densities. The paper discusses and correlates the variations in the molar refraction with density. It emerges that in different polymorphs of silica, the increase in density involves a corresponding increase in the characteristic dispersion frequencies leading to a decrease in the molar refraction. The variation of the molar refraction with density can be represented in terms of an elementary formula. The variation of the molar refraction of opals with the water content in them is also accounted for.

Keywords. Molar refraction; silica; quartz; opals; polymorphism.

1. Introduction

Silicon dioxide, referred to as silica occurs as one of the major constituents of the earth's crust and is one of the very few chemical compounds which exhibits a very large number of polymorphs (Sosman 1965). Here, we refer to all these minerals collectively as belonging to the quartz family, simply because quartz is the commonest of the several modifications of silica and also because sometimes the term silica may be understood as referring only to the amorphous or vitreous form of silicon dioxide.

The refractive indices, birefringence and dispersion of materials can throw light on the electronic absorption frequencies characteristic of the substance. Very often experimental data on electronic absorption frequencies are meagre owing to the electronic absorptions lying in the far UV region of the spectrum. Under the circumstances, the optical data provide an indirect estimate of the characteristic absorption frequencies of different substances. The refractive indices and birefringence of the various modifications of silicon dioxide have been extensively studied and a fairly exhaustive account of the mineralogy of silica is presented by Frondel (1962). Although extensive data are available on the densities and the refractive indices, a comparative study of the molar refraction of these minerals has not so far been made and the present paper brings to focus some very interesting and hitherto unrecognized features with regard to the variation of the molar refraction in these minerals. A formula is also proposed here to represent the variation of the molar refraction with density.

2. Molar refraction

The molar refraction is a measure of the electronic polarizability of the material and in isotropic substances it is defined by the relation,

$$R = \frac{M(n^2 - 1)}{\rho(n^2 + 2)} = \frac{N_A \alpha}{3\varepsilon_0}, \tag{1}$$

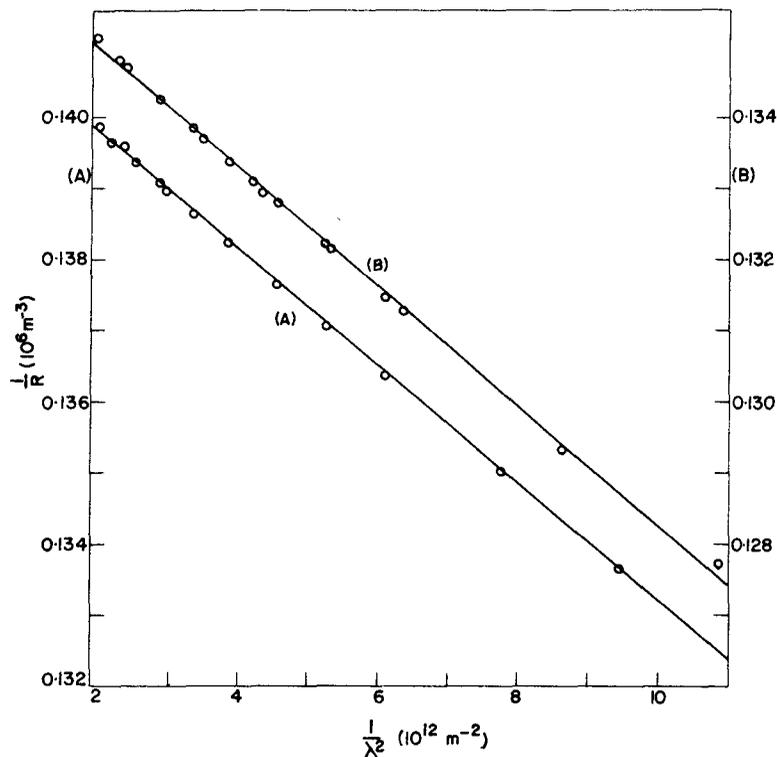where, n is the refractive index of the medium, M is the molecular weight and ρ is the

Figure 1. Dispersion of molar refraction with wavelength in (A) low quartz and (B) fused silica.

density. N_A is the Avogadro number, α is the polarizability per formula unit of SiO_2 and ε_0 is the permittivity of free space. In birefringent minerals, the average molar refraction may be calculated by replacing n^2 in (1) by the mean square of the three principal refractive indices denoted by $\overline{n^2}$. It is well known that the calculated values of the mean molar refraction in liquid, liquid crystalline and crystalline phases of most organic compounds remain practically constant (Chandrasekhar and Madhusudana 1969). This feature has its origin as stated below. The molecular structure of the individual organic molecules does not undergo any significant change due to phase transformations. The intermolecular interactions are weak and are of the van der Waals type and hence no significant changes occur in the electronic dispersion frequencies associated with the different phases. Further, in organic compounds, phase transformations involve only small changes in the density values of the material in different phases. Attention is drawn to the above facts to emphasize by contrast the entirely different nature of the situation which prevails in the different polymorphs of silicon dioxide, wherein the densities vary over a very broad range from about 1.9×10^3 to 4.28×10^3 kg/m³. Further, the structure of silicon dioxide consists of a continuous network of silicon and oxygen, and the binding is intermediate between the ionic and the covalent types. Under these circumstances, it was anticipated that the average molar refraction associated with the different polymorphs may not remain constant and this was confirmed by our calculations which are presented and discussed in the following.

3. The different polymorphic modifications and their molar refractions

Table 1 presents the essential facts with regard to the crystal system, density and principal refractive indices of the different polymorphs of silicon dioxide. Some of the modifications are isotropic and several others are either uniaxial or biaxial. Most of the modifications have a positive sign of birefringence, *i.e.* ($\varepsilon > \omega$). The only exceptions are the cases of low-cristobalite and keatite, which are uniaxial negative. Further, the birefringence values associated with different modifications are low and of the order of 0·01. The low birefringence value justifies using $\overline{n^2}$ to calculate the average molar refraction.

It may be pointed out here that in most of the modifications excepting stishovite, the coordination of the oxygens around each silicon is approximately tetrahedral. Stishovite belongs to the typical rutile structure, wherein the coordination is different.

Density and refractive index data are also available for some irradiated samples of low quartz (Weyl and Marboe 1962) and these are included in table 2 and will figure in our discussion.

As already mentioned, the molar refraction is proportional to the electronic polarizability α, which in turn may be represented by the conventional dispersion formula, (see *e.g.*, Kittel 1974), *viz*

$$\alpha = \sum_i [A_i/(\omega_i^2 - \omega^2)], \tag{2}$$

where ω is the frequency of the electromagnetic radiation. The characteristic absorption frequencies associated with the system of ions/atoms and the relative oscillator strengths are denoted respectively by ω_i and A_i.

Table 2 presents the calculated values of molar refraction R of the different polymorphs arranged in an increasing order of density. The molar refraction exhibits a systematic decrease with increase in density. The increase in the densities of the different polymorphs arises essentially as a consequence of the increasingly more efficient packing of the ions with correspondingly higher packing coefficients. In fact, the decrease in the molar refraction with increase in density, has its origin in the increase in the dispersion frequencies. Indeed, it has to be recognized that variations in both the "polarizability" of the different units of the structure and the polarization field are collectively responsible for the consolidated decrease in the molar refraction with increase in density. In this connection, it is also useful to examine whether there is a significant change in the effective dispersion frequency. This is possible for those cases for which dispersion data are available. The relevant details are presented in §4.

4. The dispersion of molar refraction

The molar refraction which is proportional to the polarizability may be represented by a dispersion formula similar to (2), *viz*

$$R = \sum_i [B_i/(\omega_i^2 - \omega^2)]. \tag{3}$$

When one is considering the dispersion of molar refraction in regions of wavelengths far away from the absorption region, it is well known that the dispersion can be

Table 1. Polymorphs of silicon dioxide.

Polymorph	Crystal system	Density (10^3 kg/m^3)	Principal refractive indices	Reference
Melanophlogite	Cubic	1·99	1·423	Cooper and Dunning (1972)
Lechatelierite	Natural glass	2·19	1·4588	CRC Handbook (1978–79)
Fused silica	Glass	2·203	1·45845	Frondel (1962)
Low tridymite	Orthorhombic	2·26	1·469, 1·470, 1·474•	Frondel (1962), CRC Handbook (1978–79)
Low cristobalite	Tetragonal	2·331	1·484, 1·487	L-B Tabellen (1975)
Keatite	Tetragonal	2·502	1·513, 1·522	L-B Tabellen (1975)
Low quartz	Hexagonal	2·6511	1·5534, 1·5442	Frondel (1962)
Coesite	Monoclinic	2·91	1·597, 1·594	Frondel (1962)
Stishovite	Tetragonal	4·28	1·845, 1·800	Kerr (1977)
High cristobalite	Cubic	2·2 (300°C)	1·486	Winchell and Winchell (1959)
High tridymite	Hexagonal	2·27 (> 168°C)	1·480	L-B Tabellen (1975), Hubner (1977)
High quartz	Hexagonal	2·53 (600°C)	1·5405, 1·5329	Frondel (1962)
Irradiated quartz		2·6501	1·5534, 1·5444	Weyl and Marboe (1962)
Irradiated quartz		2·6483	1·5530, 1·5441	Weyl and Marboe (1962)
Irradiated quartz		2·5257	1·5272, 1·5224	Weyl and Marboe (1962)
Irradiated quartz		2·2510 (~ 300°C)	1·4666	Weyl and Marboe (1962)

Table 2. Molar refraction (λ589·3 nm) and characteristic absorption wavelength of polymorphs of silica.

Polymorph	Density (10^3 kg/m^3)	Molar refraction $R(10^{-6} \text{ m}^3)$	$R_{(\text{calc.})}$ from eqn (7)	λ_i (nm)	B_i $(10^{26} \text{ m}^3/\text{sec}^2)$
Melanophlogite	1·99	7·689	7·649	79·05	
Lechatelierite	2·19	7·497	7·507	78·05	
Fused silica	2·203	7·448	7·497	77·93	42·74
Low-tridymite	2·26	7·431	7·457	77·74	
Low-cristobalite	2·331	7·400	7·408	77·58	
Keatite	2·502	7·289	7·290	77·00	
Low-quartz	2·6511	7·190	7·189	76·37	43·00
Coesite	2·91	7·016	7·016	75·57	
Stishovite	4·28	6·084	6·172	70·44	
Irradiated quartz	2·6501	7·194	7·190	76·51	
Irradiated quartz	2·6483	7·196	7·191	76·52	
Irradiated quartz	2·5257	7·279	7·274	76·95	

conveniently represented by a single term equation similar to (3). In such cases, a graphical plot of $1/R$ as a function of ω^2, exhibits a linear dependence of $1/R$ with ω^2, as exhibited in figure 1 which refers to the data on low quartz and vitreous silica. From the slope and the intercept of the straight line graph, it is possible to calculate the constants B_i and ω_i. Here ω_i corresponds to an effective average dispersion frequency characteristic of the substance from the standpoint of the dispersion at longer wavelengths far away from absorptions. The effective absorption wavelength $\lambda_i (= 2\pi c/\omega_i)$ is lower in low quartz, although the B_i values are not very different (vide table 2). The increase in the dispersion frequency or in other words, the decrease in the effective absorption wavelength is as anticipated. The B_i values, on the other hand, are almost the same, consistent with the fact that the effective number of electrons per formula unit continues to be the same in the two modifications. Dispersion data are not available for the other polymorphs under consideration and under the circumstances, it may be reasonably assumed that B_i in all these cases is the same. Using the average B_i value obtained earlier for low-quartz and fused silica ($42·87 \times 10^{26} \text{ m}^3/\text{sec}^2$), it is possible to calculate the λ_i values for other polymorphs using the available value of the refractive index/molar refraction data for the sodium D-lines. The λ_i values so calculated are given in table 2 and the values exhibit a systematic decrease of λ_i with increase of density.

It is possible to explain from elementary considerations the variation of molar refraction as a function of density. Here, it is assumed empirically from a classical approach that the force constant associated with the electronic oscillators exhibits an increase such that the increment df in the force constant due to an increment $d\rho$ in density is proportional to the force constant f and $d\rho$. Hence, it follows that

$$df/f = C d\rho, \tag{4}$$

where C is a constant of proportionality. On integration, we get

$$f = D \exp(C\rho), \tag{5}$$

where D is a constant. Hence,

$$\omega_i^2 = f/m = D \exp(C\rho)/m,$$
$$= K \exp(C\rho), \tag{6}$$

where m is the mass of the electron and $K = D/m$ is a constant.

Substituting for ω_i^2 in (3), we get,

$$1/R = (\omega_i^2 - \omega^2)/B_i = [K \exp(C\rho) - \omega^2]/B_i. \tag{7}$$

In other words,

$$\log_e(R^{-1} + \omega^2 B_i^{-1}) = \log_e(KB_i^{-1}) + C\rho. \tag{8}$$

Here, ω is the angular frequency corresponding to the sodium D-lines. The constant B_i is calculated from (3), using the available data for low-quartz. The variation of molar refraction R with density ρ is represented by (7). Therefore, a graph of $\log_e[(1/R) + (\omega^2/B_i)]$ vs ρ should exhibit a linear variation as expected according to (8). Figure 2 exhibits this feature for nine low temperature polymorphs of silica. This is verified also for irradiated samples. As already pointed out, it is only in the case of stishovite, a small but definite discrepancy of about 1·4 % is present and this may be attributed to the fact that the coordinations of the oxygens around the silicons are not tetrahedral as is the case with the other polymorphs. In high temperature modifications, viz., high cristobalite, high tridymite and high quartz, the data available correspond to different temperatures and hence any comparison of the molar refraction of these polymorphs with those of the low temperature modifications cannot be very meaningful.

Considering the fact that the different crystalline polymorphs have different crystal structures, it is indeed noteworthy that a phenomenological description of the variation
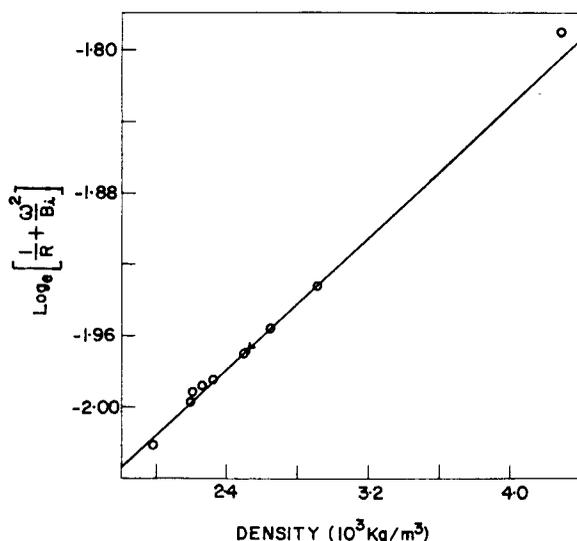
Figure 2. Functional variation of molar refraction of different polymorphs of silica with density. The circles refer to the different polymorphs given in increasing sequence of their density as in table 2. The cross refers to the irradiated sample, item 12 of table 2.

of the molar refraction with macroscopic variations in density has been possible. In fact, it only goes to prove that the molar refraction is mainly determined by the polarizability of the constituent units and on the nature of the packing of the ions.

5. Molar refraction of Opals

Opal is an aggregate of minute crystallites of cristobalite with inclusion of water in the interstices of the material (Frondel 1962a). The refractive index data for different samples of opal with different percentage composition of water are available in the literature (Frondel 1962b). The chemical formula for opal may be written as $SiO_2 \cdot (H_2O)_p$, where p is the average number of molecules of H_2O per SiO_2. If M_a and M_b are the molecular weights of silicon dioxide and water respectively and x the weight percentage of water in the opal, it follows that p and R are given by the following expressions

$$p = xM_a(100 - x)^{-1} M_b^{-1},\tag{9}$$

and

$$R(\text{opal}) = R(\text{crist}) + p \cdot R(\text{water}).\tag{10}$$

The calculated values of the molar refraction as a function of p shown in figure 3 exhibit a linear variation in accordance with (10). The slope of the straight line should correspond to the molar refraction of water and the intercept should correspond to the molar refraction of cristobalite. The straight line obtained by least square fit yields the value of $R(H_2O) = 3.856 \times 10^{-6} \, m^3$ and $R(SiO_2) = 7.404 \times 10^{-6} \, m^3$, in pleasing agreement with the values of $R(\text{water}) = 3.706 \times 10^{-6} \, m^3$ and $R(\text{cristobalite}) = 7.400 \times 10^{-6} \, m^3$, calculable from the index and density data of pure water and pure cristobalite. It may be pointed out that the density of the samples of opal varies between
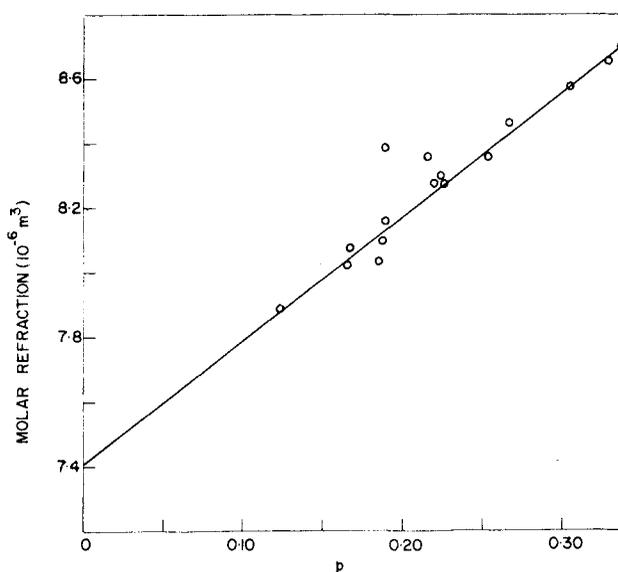
Figure 3. Variation of molar refraction of opals as a function of the molar water content.

2×10^3 and $2 \cdot 2 \times 10^3$ kg/m^3 depending on the water content. The graphical plots of density *vs* p and R *vs* density exhibit a linear variation.

Similar calculations are carried out in the case of chalcedony, another form of hydrous silica, using available data (Frondel 1982). The R (SiO$_2$) value, calculated from a least square fit of R *vs* p (which is linear) is equal to $7 \cdot 20 \times 10^{-6}$ m^3, in close agreement with the molar refraction value of low quartz, *i.e.*, $7 \cdot 19 \times 10^{-6}$ m^3. Indeed, this is consistent with the view that chalcedony is made up of aggregates of microcrystalline low quartz with inclusion of water.

6. Variation of molar refraction of low-quartz with temperature

Various investigators have discussed the thermo-optic behaviour of different minerals including low quartz, high quartz and fused silica (see *e.g.* Ramachandran 1947; Chandrasekhar 1951; Ramdas 1952). They were concerned with the variation of the electronic dispersion wavelengths associated with the variation of $(n^2 - 1)$ with temperature and it was recognized that the absorption frequencies decrease with increase of temperature. However, we are concerned with the variation of molar refraction with temperature. Data are available on the refractive indices of quartz at various temperatures (Frondel 1962c). The density values at various temperatures are calculable from the data on thermal expansion of quartz (AIP Handbook 1972). Using these data the molar refraction values of quartz are calculated, for different temperatures. The molar refraction increases with increase of temperature. However, the increase in molar refraction with temperature is somewhat larger than what may be expected as due to a mere decrease in density according to (7). The more rapid increase in molar refraction may be understood only in terms of the greater interactions between the lattice vibrations and the electronic motion, at the higher temperatures.

An analogous increase of molar refraction with increase in temperature is also exhibited by fused silica. Table 3 exhibits the variation of molar refraction with temperature, in low quartz and fused silica.

Table 3. Variation of molar refraction with temperature.

Quartz			Vitreous silica		
Temperature (°C)	Density (10^3 kg/m^3)	Molar refraction $R(10^{-6}$ m$^3)$	Temperature (°C)	Density (10^3 kg/m^3)	Molar refraction $R(10^{-6}$ m$^3)$
−140	2·6631	7·1655	−160	2·2030	7·4295
−45	2·6565	7·1819	−64	2·2031	7·4418
23	2·6507	7·1954	18	2·2029	7·4534
115	2·6412	7·2158	130	2·2026	7·4729
212	2·6307	7·2395	235	2·2021	7·4926
305	2·6180	7·2639	365	2·2016	7·5181
410	2·6012	7·2945	475	2·2012	7·5418
550	2·5630	7·3519	590	2·2008	7·5640
580	2·5350	7·3842	1000	2·1995	7·6605
650	2·5355	7·3965			
765	2·5362	7·4113			

7. Conclusion

From the foregoing discussion, it may be concluded that the significant changes associated with the densities of the different polymorphs of silicon dioxide clearly involve an increase in the characteristic dispersion frequencies leading to a corresponding decrease in the molar refraction with increasing density, according to the formula proposed.

Acknowledgement

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