

GLADSTONE - DALE CONSTANTS FOR H₂O AND CO₂ IN CORDIERITE

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ABSTRACT

Calculation of the Gladstone-Dale constants k for channel H₂O and CO₂ in a cordierite yield values (0.298 and 0.272, respectively) that differ markedly from those (0.340 and 0.211, respectively) cited by Mandarino (1976). Within the unusual structural environment afforded by channels in cordierite, molecular H₂O and CO₂ evidently possess electron polarizabilities that differ significantly from those that these oxides exhibit in the materials studied by Mandarino.

Keywords: Gladstone-Dale constants, cordierite, channel H₂O, channel CO₂.

SOMMAIRE

Les valeurs calculées de la constante k de Gladstone-Dale pour les molécules de H₂O et de CO₂ dans les canaux de la cordiérite (0.298 et 0.272, respectivement) diffèrent fortement de celles que cite Mandarino (1976) (0.340 et 0.211, respectivement). Il est évident que la polarisabilité électronique des molécules dans le milieu structural inusité de ces canaux diffère beaucoup des valeurs qu'elles possèdent dans les composés étudiés par Mandarino.

(Traduit par la Rédaction)

Mots-clés: constantes de Gladstone-Dale, cordiérite, H₂O des canaux, CO₂ des canaux.

INTRODUCTION

In the Gladstone-Dale relationship

$$K = \frac{n-1}{d} = \frac{k_1 p_1}{100} + \frac{k_2 p_2}{100} \dots \frac{k_i p_i}{100} \dots \quad (1)$$

K represents the specific refractive "energy" for a substance with index of refraction n and density d , whereas $k_1, k_2 \dots k_i$ represent the specific refractive "energies" and $p_1, p_2 \dots p_i$ represent the weight percentages of the i components that comprise this substance. Donnay

et al. (1980) recommended replacing the term *specific refractive energy* with the term *specific refractivity*, and Mandarino (1981) suggested that the constants $k_1, k_2 \dots$ be called Gladstone-Dale constants. Mandarino (1978) also proposed that the symbol K_P represent the value for K calculated (equation 1) from the material's physical constants, namely, $K_P = (n - 1)/d$, and that K_C represent K calculated from the material's chemistry and Gladstone-Dale constants, namely,

$$K_C = \frac{k_1 p_1}{100} + \frac{k_2 p_2}{100} \dots$$

Using data from the Tutton salts and other pure synthetic compounds, Mandarino (1976, 1978, 1981) calculated new Gladstone-Dale constants for 129 constituents, largely oxides, and compared these with Larsen's (1921) values. In neither set do the constants for H₂O and CO₂ compare with those calculated by the writers for H₂O and CO₂ lodged within the channels of cordierite. Evidently, the degree of electron polarization (by visible light) of channel H₂O and CO₂ differs significantly from that exhibited by these oxides in the Tutton salts and synthetic compounds studied by Mandarino. This finding illustrates that structural environment may significantly modify the contribution of a particular oxide component to a substance's index of refraction and, hence, may modify the oxide's Gladstone-Dale constant for this substance. Gladstone-Dale calculations for minerals may consequently be improved in accuracy if a constant is used that is more commensurate with the oxide's structural environment in the mineral (rather than the all-purpose constants, which are presently the only ones available).

EXPERIMENTAL

To calculate the Gladstone-Dale constants

for H₂O and CO₂, both known (from IR spectra) to be present as molecules in the channels in cordierite, the writers held inclusion-free 200 μm grains of a cordierite from White Well, Australia (Pryce 1973) at 1200 to 1300°C for 24 hours in a SiC furnace. This expelled the volatile occupants of the channel without destroying the cordierite structure. Microprobe analyses and H₂O and CO₂ determinations indicate the formula of this cordierite to be, before heating, K_{0.00}Na_{0.05}(Mg_{1.94}Fe_{0.08}Mn_{0.01})Al_{3.97}Si_{4.99}O₁₈[0.33H₂O, 0.08CO₂] and, after heating, K_{0.01}Na_{0.05}(Mg_{1.91}Fe_{0.09}Mn_{0.01})Al_{3.98}Si_{5.01}O₁₈.

H₂O or CO₂ was reintroduced into the channels of some of the channel-evacuated grains by sealing these grains in platinum tubes and holding them at 600°C for 4 weeks (1) at H₂O pressures of 0.5, 2.0, 4.0 and 6.0 kbar or (2) at CO₂ pressures (from decomposition of Ag₂C₂O₄) of 2.0, 4.0, 5.0, and 6.0 kbar. For these grains, indices of refraction for sodium light were determined to within ±0.0005 using the double variation method in conjunction with a Supper spindle stage (Bloss 1981). For these same grains, unit-cell dimensions were determined by transfer of the goniometer head containing the grain to a back-reflection Weissenberg camera. Values of 2θ for at least 60 indexed reflections (CuKα₁, CuKα₂ and CuKβ) were submitted to the least-squares program of Burnham (1962, 1965), revised by L. Finger, which corrects for systematic errors in film shrinkage, absorption and eccentricity.

The amount of channel H₂O in the treated grains was quantitatively determined using the equation of Medenbach *et al.* (1980). CO₂ in the samples was analyzed coulombmetrically using the technique (and equipment) of Johannes & Schreyer (1981).

RESULTS AND CALCULATIONS

From the empirical data thus determined (Table 1), we calculated (1) the mean index of refraction for sodium light [$\bar{n} = (\alpha\beta\gamma)^{1/3}$] and also (2) the density *d* for each grain studied. Thus, density was calculated from the equation

$$d = \frac{MZ}{V} 1.6602 \text{ g cm}^{-3} \dots \dots \dots (2)$$

where *V* represents the unit-cell volume in cubic ångströms, *M* is the molecular weight corresponding to the chemical formula of the crystal, and *Z* represents the number of formula units in the unit cell, namely 4 for cordierite. The value of *M* for the channel-evacuated cordierite grain was determined to be 589.18 using the after-heating formula already given. In calculating the density of a hydrated or carbonated grain, however, this value for *M* was multiplied by 100/(100-*p*), where *p* represents the weight percent of H₂O or CO₂ present in the grain. Substituting these values for *M* into equation 2, plus the unit-cell volumes already determined, the densities cited in Table 1 were calculated.

Using the mean index of refraction \bar{n} , *K_F* was calculated for each grain studied (Table 1).

TABLE 1. GAS CONTENTS, INDICES, CELL VOLUMES, CALCULATED DENSITIES, AND *K_F* VALUES

Wt. % gas	Refractive indices*				<i>V</i> (Å ³)	<i>d</i> calc	<i>K_F</i>
	α	β	γ	\bar{n}			
Channel-evacuated cordierites							
—	1.5235	1.5254	1.5275	1.5255	1550.5	2.524	0.2082
H ₂ O-treated cordierites							
1.05 H ₂ O	1.5303	1.5340	1.5362	1.5335	1550.6	2.553	0.2090
1.68 H ₂ O	1.5351	1.5389	1.5410	1.5383	1550.4	2.567	0.2097
2.24 H ₂ O	1.5386	1.5440	1.5450	1.5425	1550.6	2.581	0.2102
2.56 H ₂ O	1.5409	1.5465	1.5477	1.5450	1550.1	2.591	0.2104
CO ₂ -treated cordierites							
0.91 CO ₂	1.5263	1.5305	1.5345	1.5304	1550.8	2.546	0.2083
1.88 CO ₂	1.5326	1.5381	1.5459	1.5389	1550.5	2.572	0.2095
2.61 CO ₂	1.5362	1.5410	1.5525	1.5432	1551.1	2.590	0.2097
3.13 CO ₂	1.5388	1.5446	1.5582	1.5472	1551.8	2.603	0.2102

*For wavelength 589.3 nm.

For example, for the channel-evacuated grain we obtain

$$K_{P, \text{ee}} = \frac{\bar{n} - 1}{d} = \frac{1.5255 - 1}{2.524} = 0.2082.$$

and for the grain containing 2.56 wt. % H₂O,

$$K_{P, 2.56\text{H}_2\text{O}} = \frac{1.5450 - 1}{2.591} = 0.2104$$

For this second grain, the Gladstone-Dale relationship (Eq. 1) indicates

$$0.2104 = 0.2082 \frac{97.44}{100} + k(\text{H}_2\text{O}) \frac{2.56}{100}$$

Solving this equation for $k(\text{H}_2\text{O})$, the Gladstone-Dale constant for channel H₂O in cordierite, we obtain 0.294. Similar calculations involving the data from other grains yielded several values for $k(\text{H}_2\text{O})$ and for $k(\text{CO}_2)$ (Table 2). The grains containing the least amounts of H₂O or CO₂ likely yielded the least reliable values. The value of 0.219 for the specific refractivity of channel CO₂ in cordierite seems particularly divergent even though it compares best with the values 0.211 and 0.217, given by Mandarino (1981) and Larsen (1921), respectively. Excluding this value, the average for $k(\text{CO}_2)$ is 0.272. The excess of this value over those given by Mandarino and Larsen probably results from the linearity of the CO₂ molecule in the channels of cordierite. Such linearity may increase the polarizability of the oxygens involved, so that higher indices of refraction result. By contrast, our average value for $k(\text{H}_2\text{O})$, namely 0.298, is less than the value of 0.340 that Mandarino and Larsen report. This value of 0.298 perhaps indicates a greater structural isolation of H₂O in the channel of cordierites than in the crystals that yielded the data of Larsen or Mandarino. Armbruster & Bloss (1982) describe in detail the effect of the orientation of channel H₂O and CO₂ molecules on the optical properties of cordierite.

A difficulty in calculating k , the Gladstone-Dale constant, for a minor component such as channel H₂O or CO₂ in cordierite, is that small errors in the quantitative determination of this component may represent a relatively large percent of this minor component. Hence, these small errors may propagate appreciable errors in the values of k thus calculated. On the other hand, in compounds consisting almost entirely of this component, for example, water or ice in the case of H₂O, the structural environment differs markedly from those in which this component is minor.

TABLE 2. CALCULATED GLADSTONE-DALE CONSTANTS FOR CHANNEL H₂O and CO₂ IN CORDIERITE

Wt. % gas		Calculated Gladstone-Dale constants	
H ₂ O	CO ₂	$k_{\text{H}_2\text{O}}$	k_{CO_2}
1.05		0.303	
1.68		0.297	
2.24		0.298	
2.56		0.294	
	0.91		0.219 (?)
	1.88		0.277
	2.61		0.266
	3.13		0.272

The Gladstone-Dale constants in Table 2 entail approximately the same percent error (but opposite in algebraic sign) as that present in the H₂O or CO₂ determinations. With respect to these results, Medenbach *et al.* (1980) cited, for H₂O determined by their method, an *esd* of 0.13 wt. %. Consequently, for cordierites containing 1 wt. % H₂O or less, Gladstone-Dale constants in error by more than 10% might result. For the CO₂ determinations, Johannes & Schreyer (1981) have estimated the error to be within $\pm 3\%$ of total CO₂ for CO₂ contents of about 1 wt. %. However, unlike the H₂O determination, which in effect is performed on the crystal whose indices of refraction and cell edges were measured, the CO₂ analysis is performed on a sample of many grains and then applied to the crystal studied optically and by X-rays. Disparity between the CO₂ content of this crystal and that of the sample analyzed may introduce additional error into the Gladstone-Dale constants calculated for the crystal.

CONCLUSIONS

The accuracy of Gladstone-Dale calculations for minerals will increase if Gladstone-Dale constants become available that are appropriate not only to a constituent but to its environment in the mineral. The calculated k values for channel H₂O and CO₂ in cordierite appear to have acceptable precision, but further tests of their accuracy may be advisable through study of additional cordierites.

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